REACTION KINETICS OF TEXTILES

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

by

William Edgar Giddens

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Mechanical Engineering

Georgia Insititue of Technology

March, 1973

REACTION KINETICS OF TEXTILES

Wolfgang Wulff, Chairman

P. Durbetaki

E. C. Ashby

Date Approved by Chairman 3/8/1973

ACKNOWLEDGEMENTS

I would like to extend my appreciation and thanks to my thesis advisor, Dr. Wolfgang Wulff, for his suggestion of the problem dealt with in this study and for his helpful suggestions and advice given during the duration of this work.

I would also like to thank the School of Chemistry at the Georgia Insititute of Technology and expecially Dr. E. C. Ashby for the use of the Mettler Thermoanalyser 2 employed during the course of this study. Dr. P. Claudy's assistance is also acknowledged with great appreciation.

Especially, I thank my wife, Dianne, who has stood by me in this work.

I also thank the National Science Foundation for funding this research under grant GI-31882.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

SUMMARY

The problem of fabric flammability has lead the Congress of the United States to initiate research under the auspices of the Government-Industry Research Committee on Fabric Flammability with the purpose of setting reasonable fabric flammability standards and criteria. The Fire Hazard and Combustion Research Laboratory, under the direction of Dr. W. Wulff, at the Georgia Institute of Technology's School of Mechanical Engineering is now endeavoring to predict the fabric ignition time. This knowledge would go a long way toward the setting of reasonable flammability standards.

The fabric ignition time has been characterized as a function of fabric material properties, physical processes, and geometry. In this study the measurement and evaluation of the fabric chemical kinetic properties, namely order of reaction, activation energy, pre-exponential factor, and enthalpy of reaction was attempted. Simultaneous DTA/TGA experiments were carried out on the ten primary GIRCFF fabrics at the heating rates of 25 and 10°C per minute.

Existing methods of kinetic parameter evaluation, along with original methods, were used to evaluate the kinetic parameters for fabric moisture desorption and oxidation. A new method of analysis for heat of reaction evaluation was used to evaluate the enthalpy of moisture desorption while existing methods were used to evaluate the heat of fusion for the melting fabrics.

NOMENCLATURE

A	DTA peak area	sec.-°C
b	Regression coefficient	
B	Correlation coefficient squared	
c	Specific heat	cal./g.-°K
C	Heat capacity	cal./°K
E	Activation energy	kcal./mole
ΔH_f	Enthalpy of reaction	cal./g.
k_o	Pre-exponential factor	1/sec.
K	Overall heat transfer coefficient	cal./sec.-°K
m	Mass	g.
n	Order of reaction	
q'''	Internal heat source term	cal./g.-sec.
r	Correlation coefficient	
R	Gas constant	1.986 cal./mole-°K
s_y	Standard deviation of y	
s_z	Standard deviation of z	
s_{yz}	Standard deviation of z on y	
t	Time	sec.
T	Temperature	°K
ΔT	Differential temperature	°C
w	Mass of sample reacted	g.
x	Mass fraction reacted	

NOMENCLATURE (Concluded)

$\dot{x}$	Time rate of change of mass fraction	1/sec.
Greek Symbols		
α	Thermal diffusivity	$cm.^2/sec.$
Δ	Difference	
λ	Thermal conductivity	cal./cm.-sec.-°K
ρ	Density	$g./cm.^3$
ϕ	Heating rate	°C/min.
Subscripts		
c	Crucible	
f	Furnace	
g	Gold powder	
m	Maximum rate state	
r	Reference	
s	Sample	
o	Initial state	
∞	Final State	

CHAPTER I

INTRODUCTION

Description of the Problem of Fabric Flammability

Clothing and fabric fires cause the death of between 3,000 to 5,000 persons, non-fatal burn injuries to approximately 200,000 more, and property damage in excess of 250 million dollars in the United States each year [1]*. Fabric flammability is not a recent phenomenon, but has been a national problem for years. The "torch" sweaters of the 1950's are one example out of many. Although legislation dealing specifically with highly flammable fabrics has been in existence for many years, it has only been within the past five years that any tangible move toward fighting the menace of fabric flammability has been made.

The Congress, in 1967, amended the Flammable Fabrics Act of 1953 so as to direct the Secretary of Commerce to establish reasonable criteria or standard tests to be applied to fabrics to protect the public from the excessive hazards of fabric related burn injuries. In order that reasonable criteria be legislated, the technical and scientific knowledge necessary to do so must first be available. This knowledge is now being gathered through research programs sponsored jointly by the United States textile industry and the United States Government. These research programs are administered by the authority of the Government - Industry Research Committee on Fabric Flammability (GIRCFF).

---

*Numbers in brackets refer to the Bibliograghy.

The basic problem of fabric flammability studies can be summed up in the statement made in support of the Flammable Fabrics Act by the Government - Industry Research Committee [2]: "The determination of the relationship between fabric behavior in a test method, on the one hand, and the hazard it presents in actual use, on the other, is necessary in order to develop meaningful standards."

Relevance of the Research

The Department of Mechanical Engineering at the Georgia Institute of Technology is carrying out research on the problem of fabric flammability under the auspices of the Government - Industry Research Committee and supported by the National Science Foundation under the RANN program (Research Applied to National Needs). The research is being carried out in the Fire Hazard and Combustion Research Laboratory under the Principal Investigator Dr. Wolfgang Wulff.

Fabric flammability research at the Georgia Institute of Technology is based on the proposal of Tribus [3] that the relation between the behavior of fabrics in a laboratory experiment and the hazard it presents in actual use, can be formulated in terms of probabilities. The two probabilities considered to be of particular importance are (1) the probability of ignition given exposure, P(I/E), and (2) the probability of burn injury given ignition, P(B/I). The GIRCFF [2] considers it of primary importance to "determine what properties of a fabric are important in determining the values of P(I/E) and P(B/I)."

It has been shown by Evans et al. [4] how modeling analysis and experiments can be used to obtain the probabilty of ignition P(I/E) as well as the probability of burn injury P(B/I). It was also shown that

the probability of ignition, P(I/E), curve can be obtained and expressed in terms of (1) physical properties and dimensions of the fabric material, (2) physical processes such as heat and mass transfer, etc., and (3) human responses and reaction [4].

The probability of ignition, P(I/E), and the resulting flammability standards must ultimately be defined on the basis of modeling experiments since laboratory controlled and instrumented experiments on humans are impossible. The model used must present a reasonable facsimile to the conditions found on the human prototype, so as to produce all the necessary parameters to completely describe the characteristic fabric properties of ignition and burning and the process parameters. Wulff et al. [5] state the fabric conditions which must be met by the modeling analysis and the techniques needed:

> The processes characterizing flammability are essentially transient in nature. Considering pertinent times, the probability of ignition for given exposure should depend primarily on the ratio of the time a person exposes the fabric to a heat source to the time required for ignition. The exposure time can be at most stochastically related to the fabric characteristics, and this doubtful relation is as yet to be established, while the ignition time depends strongly and deterministically on fabric properties. Hence, fabric characteristics being the objective, the problem becomes that of predicting the ignition time for a given set of circumstances.

The all important ignition time is determined by a partial modeling analysis which takes into account (1) fabric material properties, (2) physical processes such as heating modes and boundary conditions, and (3) different geometries. Consistent with the objective of predicting the ignition time, the partial modeling analysis must include the four partially overlapping stages which characterize the response to

heating as proposed by Wulff et al. [5]:

(a) inert heating of the fabric

(b) thermal decomposition, change in shape, drying accompanied by the evolution of combustible, and non-combustible gases, smoke with entrained solid particles, or by melting and shrinking

(c) Ignition, that is the appearance of a flame as evidence of exothermal reaction by the volatiles, or the onset of smoldering.

(d) combustion, char formation.

The fabric properties which are necessary in the modeling description are the fabric density, specific heat, temperature, radiative properties, and the chemical reaction parameters. The governing equations are the equations of energy conservation for the fabric interior and the fabric surfaces and the chemical reaction equations which lead to a model of one dimensional heat transfer, simultaneously by conduction and diffuse radiation, with internal heat source. The fabric density, specific heat, radiative properties, and ignition temperature have been measured previously at the Fire Hazard and Combustion Research Laboratory at the Georgia Institute of Technology under Dr. Wolfgang Wulff [5]. The objective of this thesis is to provide the necessary chemical reaction parameters needed to complete the modeling analysis and thereby predict fabric ignition times. With the fabric ignition time determined, reasonable flammability standards will follow.

The fabrics of interest follow, at least sectionally, the well-known nth-order Arrhenis - type decomposition law

$$\frac{dx}{dt} = (1 - x)^n \; k_o e^{-E/RT}. \qquad (1)$$

Equation (1) forms the basis of the internal heat source term, $q'''(T)$, which is found in the fabric conservation of energy equation and is defined as follows

$$q'''(T) = (\Delta H_f) \; (1 - x)^n \; k_o e^{-E/RT} \qquad (2)$$

The parameters which this thesis seeks to provide are the order of reaction, n, the activation energy, E, the pre-exponential factor, k_o, and the enthalpy of reaction, ΔH_f, with special emphasis on the pryolysis. The chemical reaction parameters will be sought for the ten Primary GIRCFF Fabrics which include selected cotton, polyester, nylon, and acetate fabrics and blends as listed in Appendix A.

Advances Needed

The measurement of the chemical kinetic parameters of polymeric materials including fabrics has generally been dealt with in the area of physical analysis known as thermal analysis. Previous investigators [6] have found the kinetics of the thermal degradation of polymers by measuring the change in weight of the polymer over a series of constant temperatures. This technique is known as isothermal or static gravimetric analysis. The study presented here, however, employed dynamic thermogravimetric analysis or TGA, which allows the determination of the kinetic parameters desired from a single experimental curve. While

the kinetic parameters of n, E, and k_o can be obtained from a thermogravimetric trace, the heat of pyrolysis lends itself to being evaluated by differential thermal analysis or DTA which is described below along with TGA.

This study has sought to provide the heat of pyrolysis and the kinetic parameters of the ten Primary GIRCFF Fabrics by employing the method of simultaneous DTA and TGA. A comprehensive literature search was also performed in order to compare the techniques and results of previous investigators with this study.

Experimental Approach

The following sections deal with the objectives and descriptions of differential thermal analysis and thermogravimetric analysis.

Objectives of Differential Thermal Analysis

A concise definition of DTA, as given by Mackenzie [7], is given below:

> Differential thermal analysis is a technique of recording the difference in temperature between a substance and a reference (inert) material as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. The record obtained is called the differential thermal or DTA curve, and provided the substance is thermally active in the temperature range used, shows a series of peaks, the position of which is determined by the chemical composition and crystal structure of the substance and the area of which is related to the energy involved in the reaction occurring.

Previous works, including that of Mackenzie [7] and Borchardt and Daniels [8], have shown that the DTA area is proportionally related to the energy or enthalpy evolved in the reaction. This study will employ this theory and use it in calculating the heat of pyrolysis of

the fabrics of interest.

Objectives of Thermogravimetric Analysis

Thermogravimetric analysis involves the continuous determination of the change in sample weight as a function of time and temperature [9]. The sample is subjected to conditions of continually increasing temperature linearly with time in the same manner as DTA. Changes in weight are automatically recorded to yield a curve, usually of stepped or "S" shaped configuration, on a plot of weight fraction reacted versus time. Thermogravimetric curves show the discrete zones over which a reaction is taking place and because they are quantitative, they permit the unknown kinetic parameters in the Arrhenius equation to be evaluated. The evaluation of the kinetic parameters will be performed using methods previously proposed by Akita and Kase [10] and Freeman and Carroll [11] and an original method derived in this study.

CHAPTER II

LITERATURE REVIEW

The literature review in this section is divided into two main sections, namely literature on DTA and literature on TGA. This division was made due to considerations which are particular to each method of analysis regardless of the fact that simultaneous DTA/TGA was used in this study.

Differential Thermal Analysis

The literature review of DTA is divided into the review of DTA techniques and DTA results.

Techinques

The review of literature on techniques is divided into two parts: (1) those works which were of use in the experimental effort of this study and (2) those works which were of use in the analytical effort.

Experimental Techniques. Differential thermal analysis experiments consist of recording the temperature difference between a sample of interest and an inert reference material as illustrated in Figure 1, both subjected to the same environment, which is being heated or cooled at a predetermined rate. The differential temperature is then used to infer the reaction enthalpy. The basic components of the DTA apparatus are the sample and reference material containers and support, the differential thermocouple which senses teh difference between sample and reference temperature, the furnace which imposes the environmental

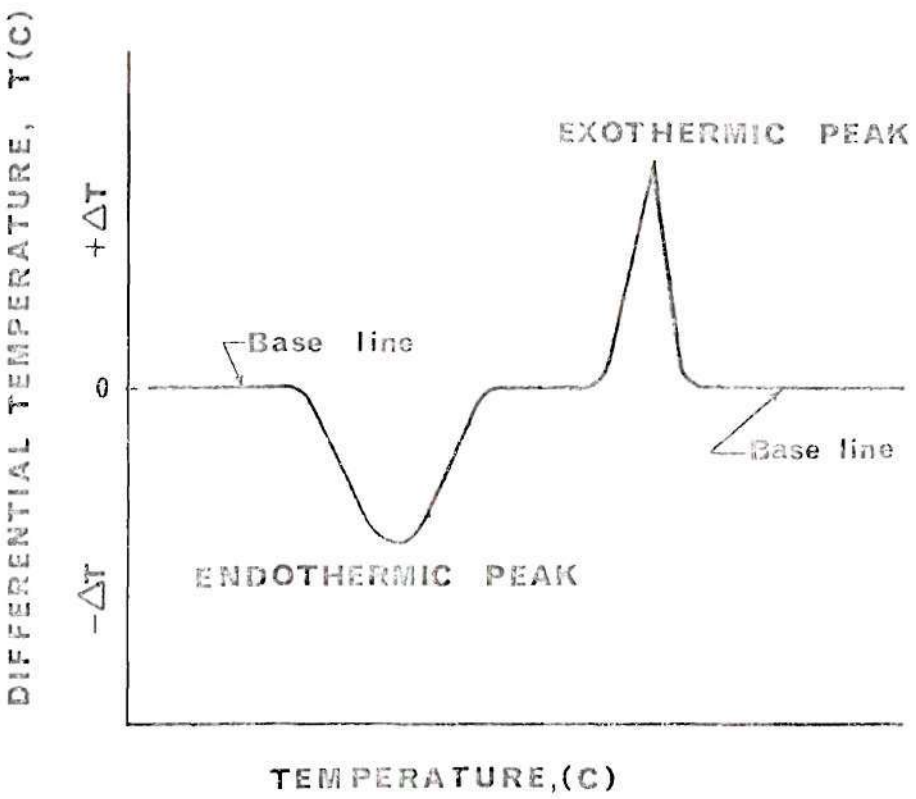


Figure 1. Idealized Thermogram for DTA.

temperature, the furnace temperature programmer, the atmosphere control, and the recording facility.

The origins of differential thermal analysis began with LeChatelier [13] in 1887. He was interested in the response of clays to heating by determining directly the rate of temperature change dT_s/dt of the material in terms of its temperature T_s. The temperatures were measured by a platinum/platinum 10% rhodium thermocouple and a photographic method was used in recording heating-curve data. In 1899 Roberts-Austen [14] advocated the use of a neutral body so as to eliminate the effects of furnace temperature variation. He modified the apparatus of LeChatelier to give the difference in temperature between the sample and neutral body ($T_s - T_r$) directly instead of by computation. The apparatus of Roberts-Austen was subsequently simplified by Carpenter and Keeling [15, 16] and by Burgess [17, 18] into the arrangement that is commonly used today. In 1909, the Leeds and Northrup Company marketed the first automatic recorder [19] which replaced the earlier photographic methods. This mechanical recorder traced directly the $T_s - T_r$ versus T_s curve by means of a double galvanometer system. Descriptions of DTA apparatus being presently marketed in this country may be found in Mackenzie [7] and Smothers and Chiang [19].

Due to the large number of experimental parameters which are inherent in DTA, any procedure has to be considered carefully in order that meaningful results might be obtained. The parameters of concern include reference material, sample size and texture, dilution of sample, heating rate, thermocouple and thermocouple position, and atmosphere

control, as considered below.

(1) Reference Material. Smothers and Chiang [19] consider the reference material to be as important as the sample. They report that the reference material must be chemically inert during heating and that it should have thermal characteristics as similar as possible to those of the sample. Grimshaw et al. [20] have suggested the use of a pre-calcined reference material to eliminate base-line drift. In the field of textile research, powdered aluminum oxide (Al_2O_3) has been used as a reference material by Schwenker et al. [9], Akita and Kase [10], Godfrey [21], Loughlin et al. [22], Ramiah [23], and Schwenker and Zuccarello [24], while glass beads have been used by Hendrix et al. [25], Perkins et al. [26], and Tang and Neill [27].

(2) Sample Preparation. Mackenzie [7] has investigated the effect of sample particle size in DTA experiments and has claimed that the sample particle - size distribution can influence the heat transfer characteristics of the sample, that the effect of particle size on the ΔT curve will be determined by the thermal characteristics of the material itself and by those of the gas in the voids, and that the type of reaction occurring will influence the resultant effect of particle size; that is, for surface reactions and diffusion-controlled decomposition reactions, particle size would be expected to have a marked effect. Arens [28] points out that increasing the particle of the sample results in strong reactions when those reactions are accompanied by changes in weight. According to Smothers and Chiang [19], differences in sample bulk density, due to differences in packing, create differences in weight,

heat conductivity, and thermal diffusivity, α, of the sample. Arens [28] makes the following conclusions concerning sample packing:

1. Difference in density of packing are the most common cause of deviations from straight base lines in temperature ranges where no reactions occur.

2. Tight packing, as it is easiest to reproduce, is recommended for most cases to obtain recordings of pronounced reactions with straight base line.

3. Loose packing gives rise to faint reactions, except for oxidation

(3) Dilution. In choosing a reference material, compatibility between reference and sample materials is of utmost importance. This is obtained by matching the reference and sample thermal diffusivites. Since this matching of thermal diffusivities is difficult in actual practice, dilution of the sample with reference material has become a standard technique in DTA. In practice, it has been found by Grimshaw and Roberts [29] and Sabatier [30] in 1954 that the amount of active material should not exceed 30 percent if accuracy in quantitative work is desired. Mackenzie [7] explains that dilution reduces baseline drift and produces sharper and narrower peaks although it also necessitates the use of a higher sensitivity recorder. Dilution prevents the ejection of material during violent reactions which produce large quantities of gas, and it also prevents the loss of contact between the sample holder and materials which shrink on melting.

(4) Sample Size. Of great importance in DTA investigations is the sample size. Mackenzie [7] states that the ideal sample would be an

infinitely small sphere around the thermocouple junction since temperature gradients within the sample would be reduced to a minimum and any reaction in the sample would take place at all points simultaneously. He also states that small samples yield smaller but narrower peaks, reduce the probability of overlap between neighboring effects, and reduce base-line drift. While there is no optimum sample size for all DTA investigations, the smallest sample which produces measurable and recordable data, is considered the best according to Mackenzie [7].

(5) Heating Rate. Heating rate has been shown to effect pack height, peak width, and, for decomposition reactions, peak temperature on $\Delta T/t$ curves by Speil [31], Nagasawa [32], and Berg [33]. These authors have reported the effects of slow and fast heating rates. A slow heating rate is said to produce (1) little loose-line drift, (2) near-equilibrium conditions, (3) broad shallow peaks on $\Delta T/t$ curves, and (4) sharp small peaks on $\Delta T/T_r$ curves. A fast heating rate is said to produce (1) appreciable base-line drift, (2) conditions far from equilibrium, (3) large, narrow peaks on $\Delta T/t$ curves, and (4) large broad peaks on $\Delta T/T_r$ curves. Mackenzie [7] states that there is no optimum heating rate, but that values of 8 to 12°C per minute are commonly used. He also states the importance of obtaining a reproductible heating rate over the temperature range of interest, since a non-linearity of the $\Delta T/t$ curve leads to distortion in the shape of peaks and relative displacement of peak temperatures.

(6) Thermocouple. A differential thermocouple is used to measure ΔT. Smothers and Chiang [19] have shown that the size of the thermocouple

wires appears to be arbitrary, although theory predicts that the wires should be as small as possible. Bollin and Kerr [34] have found that to reduce the thermal capacity of the thermocouples, the bead at the junction of the two wires should be as small as practicable. It was also found that there must be no reaction between the sample and the thermocouple. Placement of the thermocouple in the sample and reference materials is of great importance, and the position of each junction of the differential thermocouple should be such that the same thermal effects are experienced by it when no reaction is occurring. Arens [28] has made the following conclusions concerning the effects of thermocouple placement:

1. Deep placement of the differential thermocouple junctions in the samples yields DTA curves with relatively strong endothermic reactions in the low-temperature ranges and flat endothermic reactions in the high ranges.

2. Exothermic reactions (in the high temperature range) are recorded best with deep placement of the differential thermocouple.

3. For most reactions, the thermocouple should be inserted in the samples without protective cover.

4. Thermocouples, fixed in the sample holders, have a great advantage with regard to reproducibility of data.

(7) Atmosphere Control. Arens [28] has made the following conclusions concerning the effect of atmosphere:

1. The composition of the furnace atmosphere affects considerably the initiation and course of reactions accompanied by changes in weight.

2. The initiation and course of dehydration reactions are influenced by the partial vapor pressure of water. The decomposition of carbonates is influenced by the partial vapor pressure of CO_2 and the oxidation reactions are influenced by the partial vapor pressure of O_2 in the furnace atmosphere.

Schwenker [35] states that to achieve the separation of oxidative and non-oxidative reactions in polymer studies, and inert atmosphere, such as nitrogen, may be used to suppress oxidation; and he [9] has shown this effect in DTA studies of textile fabrics.

Analytical Techniques. DTA may be used to find both heats of reaction and kinetic parameters.

(1) Heat of Reaction. The most useful result in quantitative DTA is that the heat of reaction of a substance which may be evaluated from a knowledge of the area under its DTA thermogram peak. Borchardt and Daniels [8] have developed the most simplistic and representative analysis for theoretically proving the above statement. The conservation of energy equations are written for both sample and reference crubible, the two equations being identical except for the difference in superscript and the presence of a chemical heat source term dH, in the sample equation. It is assumed that (1) the temperature distribution is uniform throughout the two crucibles, (2) heat is transferred by conduction alone, (3) the overall heat transfer coefficient, K, is identical for both sample and reference crucibles, and (4) the heat capacities of the two crucibles, C, are identical. Taking the difference between the two energy equations and integrating from $t = 0$ to $t = \infty$, equation (3) is obtained

$$\Delta H = \frac{KA}{} \tag{3}$$

where A represents the area under the peak of the DTA thermogram and K is the overall heat transfer coefficient.

Tsang [19], Speil and Vold [36], and Soulé [37] have reported the same result as Borchardt and Daniels while employing similar methods of analysis. Mackenzie [7] has also obtained equation (3) but has presented correction terms for changes in sample specific heat and density with temperature. He states that the calibration constant in equation (3) must be determined from DTA experiments on a sample with a well-documented heat of reaction, and in which sufficient dilution of the sample material with reference material is a necessity.

(2) Kinetic Parameters. Kissenger [38] has derived a method for evaluating the activation energy of a substance from a knowledge of only its DTA heating rate and peak reaction temperature. Equation (1) is first differentiated to find the maximum rate of change of the fabric's weight, $\dot{x}_m$, and its peak temperature, T_m; equation (1) is then integrated and combined with the value of $\dot{x}_m$ and the result is differentiated, while small values are neglected to obtain equation (4)

$$\frac{d[\ln(\phi / T_m^2)]}{d(1/T)} = -\frac{E}{R} \tag{4}$$

Equation (4) may be used to determine the activation energy, E, for a simple decomposition reaction regardless of reaction order by making differential thermal analysis patterns at a number of heating rates.

Results

The review of literature on DTA results is divided into two parts: (1) those works which reported only qualitative results on the differential thermal analysis of fabrics, and (2) those works which reported values of reaction enthalpy and kinetic parameters for fabrics.

Qualitative Results. Schwenker et al. [9] have shown the effect of atmosphere on nylon and cotton fibers and they have also obtained the DTA curves of nylon 6, nylon 6.6, Dacron (polyester), Orlon, Creslan, polypropylene, wool, cotton, and cotton-dacron blend in nitrogen atmosphere. Schwenker and Zuccarallo [24] have shown the effects of heating rate, sample preparation and packing, and sample size of fabric samples of Dacron, nylon 6, and polypropylene. The effects of flame retardents on cotton fabrics have been investigated qualitatively by Hendrix et al. [25] and Perkins et al. [26], while similar studies have been made by Godfrey [21] on rayon fibers.

Loughlin et al. [22] have reported the major endothermic and exothermic reactions for acetate, cotton, Dacron, Orlon, Creslon, Fortrel, Kodel, and nylon's 6 and 6.6, while also reporting the melting temperatures of Dacron 54, Dacron 64, Fortrel, Kodel, Nylon 6 and Nylon 6.6 to be 263°C, 258°C, 292°C, 228°C respectively. Ramiah [23] reports the DTA of various types of cellulose, hemicellulose, and lignin, while Turner and Johnson [39] have reported the pyrolysis of acrylic fibers in an inert atmosphere.

Quantitative Results. Tang and Neill [27] have reported the effects of flame retardents on α-cellulose. In addition, they have reported a value of 88 cal. per gram for the heat of pyrolysis of α-cellulose and values of 58 to 87 cal. per gram for the heat of

pyrolysis of α-cellulose treated with five different flame retardents. A value of -3540 cal. per gram for the heat of combustion of α-cellulose and values of -3540 to -3630 cal. per gram for the heat of combustion of the treated α-cellulose are also reported. The method used in these evaluations was based on equation (3) for which the calibration reactions were the fusion of benzoic acid, $AgNO_3$, and KNO_3 in the heat of pyrolysis studies, and was the vaporization of ammonium chloride in the heat of combustion studies. Tang and Neill also report a value of -4030 cal. per gram for the heat of combustion of α-cellulose as obtained from an ozygen-bomb calorimeter.

Gilliland and Smith [40] report the values of activation energy and heat of pyrolysis for cotton fibric as obtained from equation (3) applied to a differential scanning calorimetry (DSC) trace, which is a method similar in technique to DTA. They report the heat of pyrolysis of cotton to be 100 cal. per gram before laundry and 108 cal. per gram after laundry, and the activation energy is reported to be 64 kcal. per mole before laundry and 61 kcal. per mole after laundry.

Thermogravimetric Analysis

The literature review of TGA is divided into the review of TGA techniques and TGA results.

Techniques

The review of literature on techniques is divided into the review of experimental techniques and analytical techniques.

Experimental Techniques: Thermogravimetric analysis consists of recording the change in weight of a sample as a function of time as the

temperature of the sample environment is raised at a predetermined rate. The recorded weight loss pattern produces an "S" shaped curve, as in Figure 2, in which the horizontal portions of the graph indicate that no reaction is occurring, while a change in weight indicates that a reaction is proceeding, the maximum slope having been shown by Kissinger [38] to coincide with the DTA peak.

The main components of TGA are identical with the components of DTA except that the reference material and differential thermocouple are replaced by a recording balance and that the sample weight loss is now recorded instead of the differential temperature.

The basic method of TGA was developed by Honda [41] in 1915, its analysis potential pointed out by Guichard [42] in 1925, and its emergence as a significant analytical tool was in 1947 with the work of Duval [43]. The first important application to polymeric materials was in 1959 with the work of Anderson and Freeman [44].

The TGA curve, as the DTA curve, is affected by the experimental variables of sample size and texture, heating rate, atmosphere, thermocouple placement, and atmosphere. In the case of TGA systems, the factors of shape and design of the sample crucible or holders, the speed at which the weight change is recorded, and the balance sensitivity are of great importance and are considered by Anderson [45].

(1) Sample Size. Anderson [45] states that, as in DTA, samples of large size or large particles can produce erroneous results due to heating or cooling via heat of reaction, slow diffusion of volatile products through the sample, and thermal gradients. Newkirk [46] points

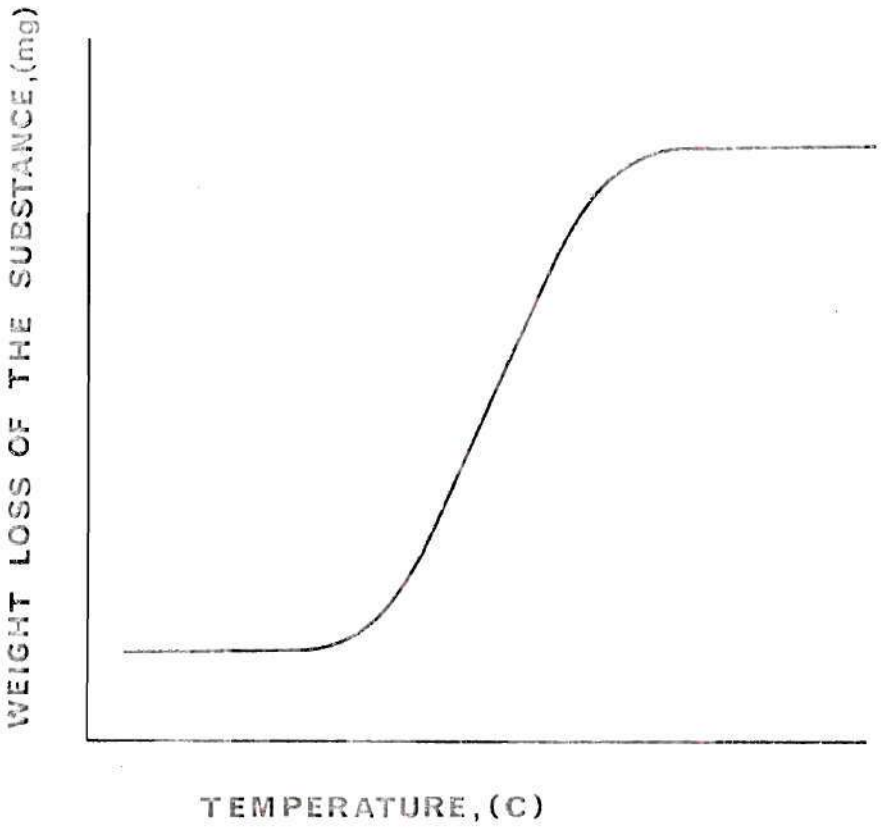


Figure 2. TGA Curve of a Simple Reaction.

out that the heat of reaction affects the difference between sample temperature and furnace temperature, causing the sample temperature to lead or lag the furnace temperature depending on the nature of the reaction. He suggests using a small sample size to minimize the heat of reaction effect, the limitations being the instrument, particularly the balance capability, and the probability of employing a representative sample.

(2) Heating Rate. Newkirk [46] has shown that, as heating rate increases, the decomposition temperature of polystyrene also increases; an effect which can significantly alter the kinetics of the reaction. Anderson [45] points out that for a two-step reaction process, a too fast heating rate may cause a step inflection to be missed. Schwenker [35] reports that heating rates of two to five °C per minute are satisfactory for quantitative purposes, while rates of up to 10°C per minute may be used for scanning purposes.

(3) Atmosphere. As in DTA, the choice of atmosphere may determine whether or not certain reactions are prevented from occurring, as shown by Schwenker et al. [9] for cotton, nylon 6.6, Orlon, and wool fabrics. Newkirk [46] reports that the atmosphere in the vicinity of the sample is constantly being changed by the addition of gaseous products which can change the composition of the atmosphere sufficiently to cause an apparent weight gain. Schwenker [35] states that spurious weight changes can also result from gas flow rates that are too rapid and that heating rates that are too rapid load to increased thermal convection resulting in apparent weight gains. It is further stated that the

magnitude of such changes may be reduced by proper venting.

The above considerations apply mainly to thermogravimetric analysis in which the change in mass of the sample is measured. Dr. R. J. McCarter [47] of the National Bureau of Standards has developed an apparatus for measuring the rate at which vapors are evolved during the thermal degradation of materials and thereby deriving the kinetics of such reactions. The apparatus yields a direct measure of reaction rate, rather than the integrated indication obtained with thermogravimetric analysis. Dr. McCarter has employed his apparatus in investigating the GIRCFF Fabrics [48] with which this study deals and his findings are treated later in this work.

Analytical Techniques. Among the many methods of analysis derived for the purpose of evaluating kinetic parameters from TGA data, three stand out as being representative of the various methods.

(1) Method of Freeman and Carroll. Freeman and Carroll [11] have developed a method which requires a knowledge of $\dot{x}(t)$ for a large number of instances during the reaction, and which yields the values on n and E simultaneously. A ratio of equation (1) written at two different instances of time is formed and the natural logarithms of both sides are taken to produce equation (5)

$$\frac{\ln(\dot{x}/\dot{x}_o)}{\ln[(1-x)/(1-x_o)]} = n - \frac{(E/R)(1/T - 1/T_o)}{\ln[(1-x)/(1-x_o)]} \qquad (5)$$

A plot of equation (5) yields a least-square line of intercept n and slope -E/R. While this method is expecially convenient, it can

introduce substantial error through the determination of $\dot{x}(t)$.

(2) Method of Coats and Redfern. Coats and Redfern [12] have derived a method which does not require a knowledge of $\dot{x}(t)$, but instead requires a knowledge of $x(t)$ for a large number of instances during the reaction. Equation (1) is integrated and natural logarithms taken to yield equation (6)

$$\ln\left\{\frac{T_o^2[1 - (1 - x)^{1-n}]}{T^2 (1 - n)}\right\} = \ln\left\{\frac{k_o R}{\phi E}\left[1 - \frac{2RT}{E}\right]\right\} - \frac{E}{RT} \qquad (6)$$

A plot of equation (6) for the correct value of n yields a straight line of -E/R.

(3) Method of Akita and Kase. Akita and Kase [10] have derived a method of evaluation which yields the order of reaction from a knowledge of the weight fraction, w_m/w_∞, at the maximum change in weight. Akita and Kase have utilized the methods of Kissenger [38] and Coats and Redfern [12] to yield equation (7)

$$[1 - (w_m/w_\infty)]^{1-n} \simeq n \qquad (7)$$

$$n \neq 1$$

where n may be found from a knowledge of w_m/w_∞. Equation (7) is especially convenient in that it requires only one set of values to be known to evaluate n, but its simplicity also leads to a lack of confidence in the results due to the possible error in finding w_m/w_∞.

(4) Other Methods. Other analytical evaluation techniques have also

been developed by Chatterjee [49], Doyle [50], Farmer [51], Reich [52], and Sharp and Wentworth [53], and are variations or additions to the above methods.

Results

The literature reviewed on TGA results is divided into qualitative and quantitative results.

Qualitative Results. The investigation of the effects of flame retardents on fabrics has been of considerable interest. Godfrey [21] has studied these effects on rayon fibers while Hendrex et al. [25] and Perkins et al. [26] have investigated the effects of flame retardents on cotton cellulose. These three studies show that the addition of flame retardents lowers the initial decomposition temperature of the fibers. Turner and Johnson [39] have investigated the pyrolysis in an inert atmosphere via thermogravimetric analysis.

McCarter [49] has investigated the GIRCFF fabrics, including nine of the fabrics investigated in this work, by the use of his apparatus which measures the rate of evolution of combustible vapors from the specimen fabrics. McCarter performed this pyrolysis on the fabric samples in a nitrogen atmosphere at a heating rate of approximately 60°C per minute, a heating rate that he believes to be sufficiently fast that the "decomposition profiles" reasonable characterize the pyrolysis behavior of the fabrics coincident with combustion. McCarter makes no evaluation of the kinetic parameters of the fabrics investigated in this work, but he does state that the rate of vapor evolution is proportional to the rate of mass loss and that the integrated area

under the rate of vapor evolution curve is proportional to the weight of sample material reacted. Due to the fact that the same fabric materials were used in McCarter's study and this study, considerable effort was expended in determining the reaction kinetic parameters from McCarter's data, and to this end is devoted a section of the chapter labeled "Results."

Quantitative Results. Thermogravimetric analysis has been used to obtain reaction parameter values of textile fabrics and fibers by a great many researchers. Many of the results found have dealt with cellulose or cellulosic materials such as cotton, while some work has dealt with thermoplastic fabrics such as polyester and nylon, and none was found dealing with fabric blends. The values of n, E, and k_o which were found in the literature are listed in Table 1 with their sources.

Table 1. Kinetic Parameters Found in Literature Survey

Fabric Description	Atmosphere	Heating Rate °C/min.	Temp. Range °C	Order of Reaction	Activation Energy kcal./mole	Pre-Exponential Factor sec^{-1}	Source*
α-Cellulose**	Vacuum	1	160-280	1	32	1.67×10^{10}	10
Cellulose R	Vacuum	4	258-282	1	36		23
ICR-1 Cellulose	Vacuum	4	300-361	1	46		23
ICR-3 Cellulose	Vacuum	4	282-361	1	47		23
α-Cellulose**	Vacuum	3	285-345	1	50.7-54.0		27
α-Cellulose	Vacuum	0.23-2.4	300-350	1	53.5	1.45×10^{17}	10
α-Cellulose	Vacuum	3	310-360	1	5.31-55.7		27
Avicel Cellulose	Vacuum	4	285-320	1	60	5.27×10^{15}	23

* Source numbers refer to Bibliography

** Indicates fabric treated with flame retardent.

Table 1 (Continued)

Fabric Description	Atmosphere	Heating Rate °C/min.	Temp. Range °C	Order of Reaction	Activation Energy kcal./mole	Pre-exponential Factor sec^{-1}	Source
Cotton Yarn	Helium	3	251-354	1	48-54		54
Cotton Yarn**	Helium	3	289-348	1	54-55		54
Cotton Cellulose	Air	5	320-380		56		9
Absorbent Cotton (ball milled)	Helium	3	245-337	1	80-86		54
Absorbent Cotton	Helium	3	265-357	1	82-86		54
Nylon 6.6	Air	5 + 10	380-480		50		9
Acetate	Vacuum	Static	180-465	1	46		55
Polyester***	Air	5	260-450	1.2	35		44
Polyester***	Air	5	450-550	1	79		44
Polyester***	Argon	5	200-450	1	20		44

*** Laminac 4116 synthetic styrenated polyester.

CHAPTER III

INSTRUMENTATION AND EQUIPMENT

The apparatus used in performing the DTA and TGA experiments in this study was the Mettler Thermoanalyzer 2, which is capable of carrying out simultaneous DTA and TGA on a single sample in an accurately defined and controlled gaseous atmosphere. The complete apparatus can be seen in Figures 3 and 4. The Mettler Thermoanalyzer was furnished by the School of Chemistry of the Georgia Institute of Technology under the supervision of Dr. E. C. Ashby.

Major Components of the Thermoanalyzer

The major components of the Mettler Thermoanalyzer 2 are the temperature programmer, furnace, balance, thermometry, sample holder, recording facility, and atmosphere control.

Temperature Programmer

The temperature programmer has a heating rate capability of from 1 to 25°C per minute and a cooling rate capability of from 1 to 10°C per minute, in intervals of one °C per minute. In addition to variable heating rates, the Thermoanalyzer 2 has the capability of employing one of five different temperature programs, namely (1) heating up to a preselected temperature, (2) heating up with isothermal holding at a preselected temperature, (3) cooling down to a preselected temperature, (4) cooling down with isothermal holding at a preselected temperature, and (5) cycling between preselected temperature limits.

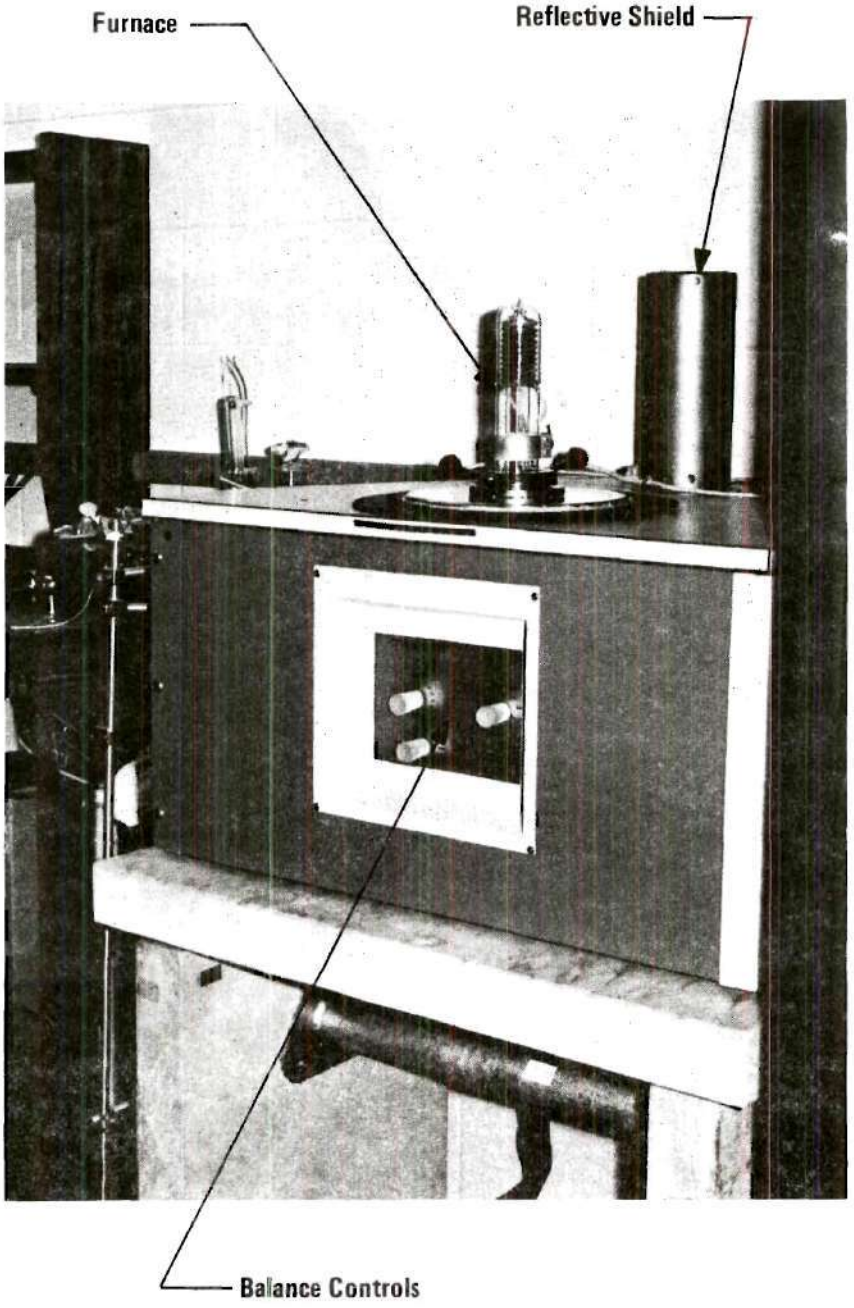


Figure 3. Balance Chamber, Furnace, and Reflective Shield.

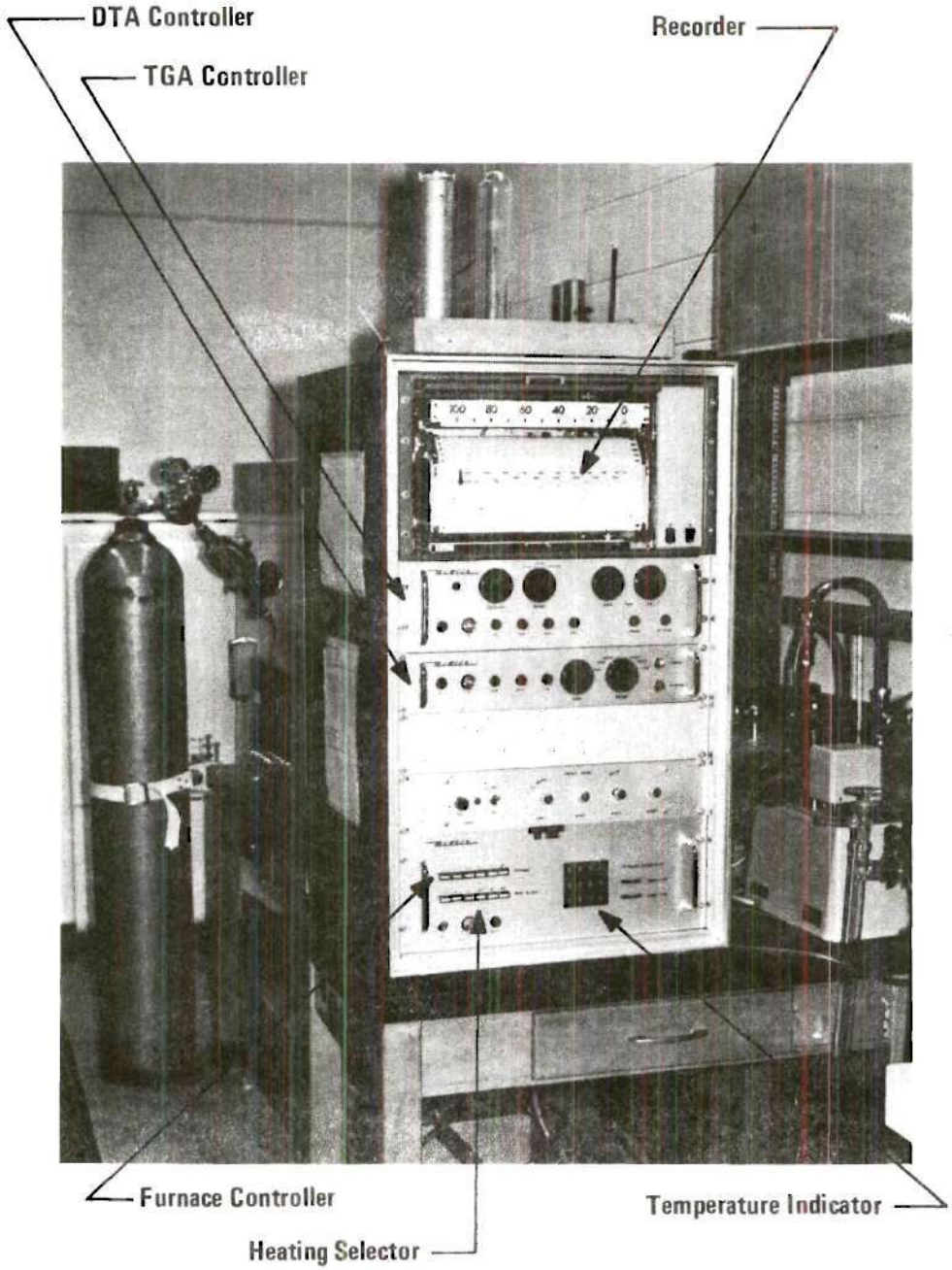


Figure 4. DTA and TGA Control Elements and Recording Facility.

Furnace

The furnace was the Mettler Middle-range Furnace System with a maximum usable heating rate capability of 25°C per minute and a temperature range of 25 to 1000°C. The Mettler furnace is a vacuum-tight quartz furnace with a bifilar kanthal heating coil and the capability of special inlets and outlets for gases. A close-up of the furnace is seen in Figure 5.

Balance

The balance used in the Thermoanalyzer was the Mettler electromagnetic compensation balance. Changes in weight cause a deflection in the balance arm from the zero position, this deflection being registered by a photocell. The deflection causes an electromagnet to compensate for the weight change to return the balance arm to the zero position. The electrical power supplied to the electromagnet is recorded as a measure of the change in weight of the sample.

The balance is built into a vacuum-tight stainless steel housing which is thermostatically controlled to assure freedom from thermal effects. All weighing adjustments, including zeroing of the balance, are performed externally, allowing the recording of weight changes without interfering with preselected environmental conditions. The Mettler weight loss amplifier incorporates two recording channels, a general channel and an expanded channel which is ten times more sensitive than the general channel. Each channel has two measuring ranges which provide a recording range of one to 100 milligrams per inch of chart paper. The Mettler balance has a capacity of 41.9 grams and

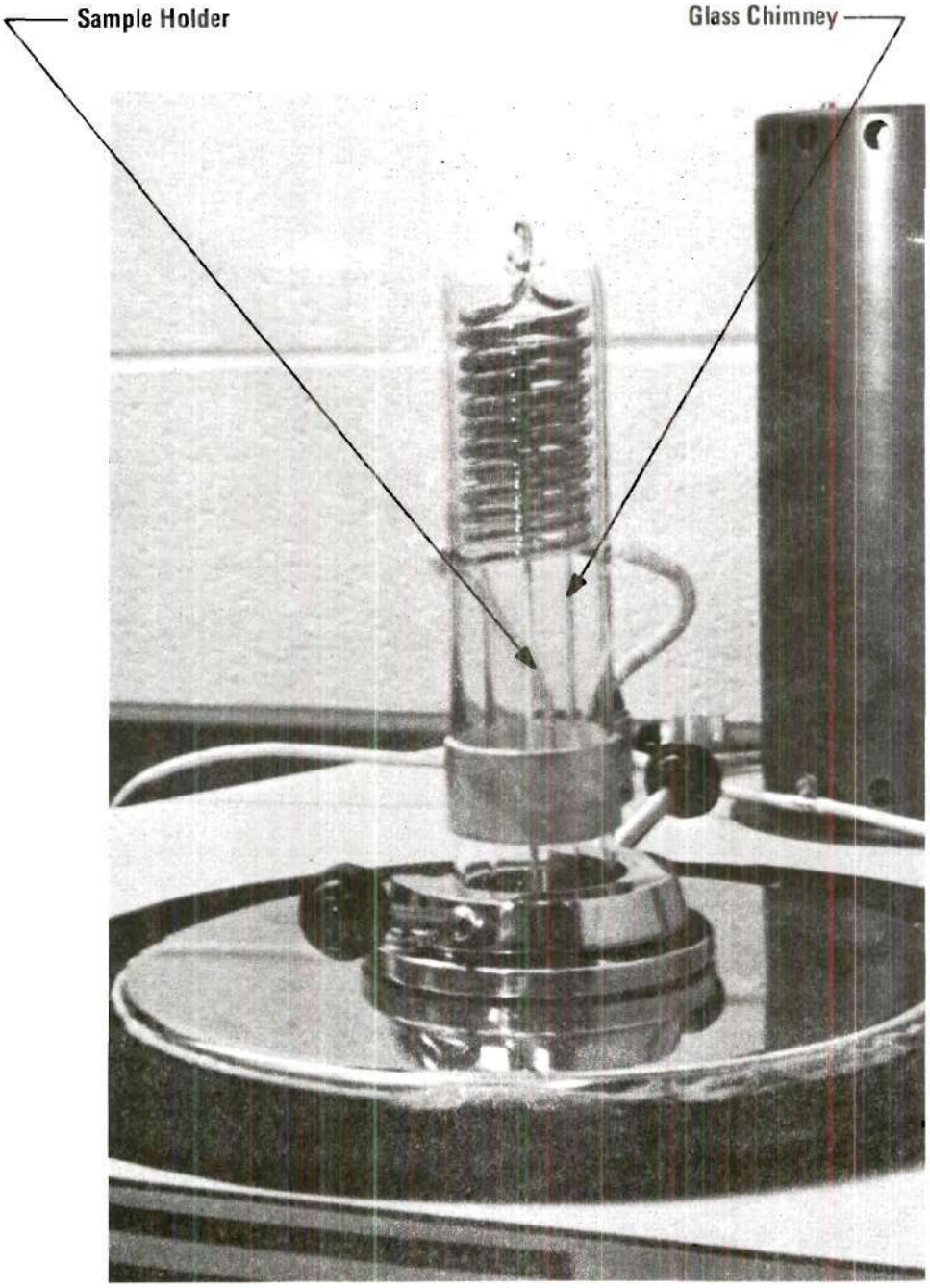


Figure 5. Close-Up of Furnace.

a standard deviation of ±0.05 milligrams in the second or higher sensitivity range.

Thermometry

The differential thermocouple used to measure the differential temperature was a platinum/platinum with 10% rhodium thermocouple. The thermocouple is located in the sample and reference holder, which is described below. The electrical connections are made by way of the plug-in nature of the sample holder in a socket attached to the balance arm. The thermocouples used in measuring the reference temperature, T_r, and in controlling the furnace temperature were also platinum/platinum with 10% rhodium.

The differential temperature amplifier was capable of recording with one of six sensitivities, namely at 2, 5, 10, 20, 50, and 100 microvolts per inch.

Sample Holder and Crucibles

The sample and reference materials were packed in platinum/10% rhodium crucibles, eight millimeters in diameter by eleven millimeters deep, as shown in Figure 6. The crucibles, supplied by the Mettler Instrument Corporation, have a volume of 0.45 cubic centimeters, the large volume being necessary due to the bulky nature of the fabrics tested.

The sample and reference crucibles, having been packed beforehand, were placed on the sample holder, which has been previously described as being mounted directly to the balance arm. The sample holder is marketed by Mettler as a "Macro TG/DTA" sample holder. The

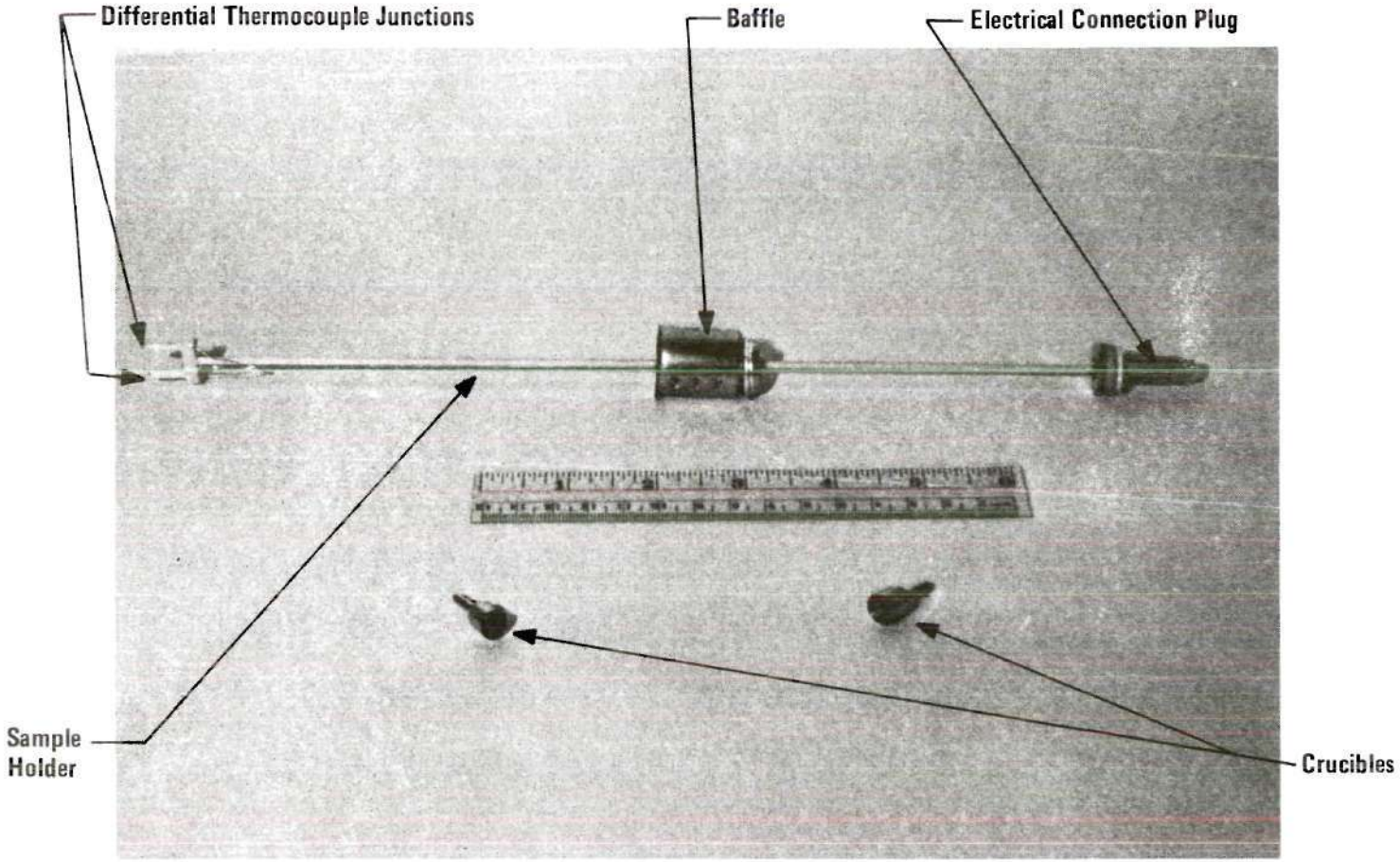


Figure 6. Close-Up of Sample Holder and Crucibles.

holder itself is made of ceramic oxide, four hole capillary tubing which, due to the fragile nature of the material, requires great care in use. The sample and reference crucibles each have a short length of tubing protruding from the bottom of the crucible which slips over a corresponding ceramic upright mounted to a ceramic cross-bar on top of the sample holder. The ceramic uprights and the sample holder stem are approximately two millimeters in diameter.

The bottom of the crucible contacts the differential thermocouple junction when the crucible is in its proper position on the sample holder. The furnace programming thermocouple is positioned in line with the holder stem and approzimately two centimeters below the ceramic crossbar. The leads of all the thermocouples pass through the sample holder stem and the electrical connections are made when the sample holder is plugged into its receptacle on the balance arm. Figure 6 shows the sample holder, thermocouple junctions, and electrical connections.

Recording Facility

The Mettler Thermoanalyzer 2 comes equipped with a six channel strip chart recording system which records all measured values on a single diagram. The printing pen records at an interval of 2.3 seconds which gives an interval of 13.8 seconds between successive points of any one channel. In this study only four channels recorded data, namely the general and expanded weight loss channels, the differential temperature channel, and the reference temperature channel. The Mettler recorder is programmed so that if the recording pen reaches

either margin, the pen is returned to the opposite margin where it continues to record. A chart speed selector feature is also found which varies chart-speed from three to 12 inches per hour. A chart speed of 12 inches per hour was used in all tests in this study.

Atmosphere Control

The dynamic atmosphere chosen for this study was air. Although an inert atmosphere would lead to simpler evaluations and more consistent results as reported by Schwenker [9, 35], it was necessary that an ozidizing atmosphere be used in order to characterize fabric combustion. The air flow was supplied by a compressed air tank and the pressure reduced through a two-stage pressure regulator, while the flow was measured with a variable area flowmeter.

The dynamic atmosphere was directed past the sample with a glass chimney, centered in the furnace, while the exhaust gases were directed between the outside of the chimney and the furnace and out of the system. The exhaust gases at no time enter the balance chamber thereby eliminating any contamination of the balance.

CHAPTER IV

PROCEDURE

The chapter on procedure is divided into the section dealing with the methods used in the experimental program and the section dealing with the analytical evaluation of the kinetic parameters.

Experimental Procedure

The section on experimental procedure is divided into the section on sample preparation and the section on test procedure.

Sample Preparation

The sample preparation, due to its large effect on DTA and TGA results, was considered carefully prior to the actual experimentation. The factors that were considered in preparing the sample were (1) reference material, (2) sample particle size, (3) dilution, (4) sample size, and (5) sample weighing and packing.

Reference Material. Three choices of reference materials were used in this study. They were (1) Fisher 80 to 200 mesh aluminum oxide (Al_2O_3), (2) Norton 60 mesh alundum (Al_2O_3), and (3) Alpha Ventron 99.9 percent pure, 100 mesh gold powder. The Fisher Al_2O_3 was subject to an approximate 10 percent loss in weight upon heating due to moisture desorption while the Norton Al_2O_3 was subject to an approximate one percent loss in weight due to moisture desorption. The gold powder reference was not subject to weight loss on heating nor was it subject to oxidation at high temperatures. Due to the samll sample sizes used

in this study, the moisture desorption of the two Al_2O_3 references introduced weight losses and thermal effects which precluded the accurate measurement of any kinetic parameters or heats of reaction; thus only the tests made with the gold powder reference were used in the kinetic data evaluation.

Fabric Sample Particle Size. The fabric samples were prepared with the work of Schwenker and Zuccarello [24] in mind, which finds a lack of reproducibility of results in finely-ground fabric samples. Fabric samples, as obtained from the manufacturer, were cut into a loose fuzz of approximately 1/16 inch length. During the preparation, the fabrics were not handled by hand and not contaminated with foreign substances. All samples were in equilibrium with 65 percent relative humidity.

The possibility of further sample size reduction was attempted by grinding fabric samples at dry ice and liquid nitrogen temperatures with a mortar and pestle. No further reduction occurred as the fabric still remained pliable even at the liquid nitrogen temperature of -196°C.

Fabric Sample Dilution. The sufficient dilution of the sample with reference material has been shown in Chapter II to be a necessity for reducing baseline drift and for obtaining useable accuracy in heat of reaction studies. In the tests made with the Fisher Al_2O_3, no dilution was made due to the large percentage of weight loss experienced by the Al_2O_3. The dilution ratio in the tests made with the Norton Al_2O_3 was approximately 10 percent fabric material and 90 percent refer-

ence material in the sample crucible. The dilution in the tests made with the gold powder reference was approximately 20 percent fabric material and 80 percent reference material in the sample crucible.

Fabric Sample Size. In keeping with the recommendations on sample size found in Chapter II, sample sizes used in the Fisher Al_2O_3 reference tests were approximately 10 milligrams Al_2O_3 in the reference crucible and 10 milligrams fabric material in the sample crucible. In the tests made with the Norton Al_2O_3, the reference crucible contained approximately 100 milligrams Al_2O_3 while the sample crucible contained 10 milligrams fabric material and 90 milligrams Al_2O_3. In the tests made with the gold powder reference, the reference crucible contained approximately 100 milligrams gold powder while the sample crucible contained 20 milligrams fabric material and 80 milligrams gold powder reference material.

Fabric Sample Weighing and Packing. The sample and reference crucibles were prepared by first weighing the empty sample and reference crucibles. Sample and reference materials were then added to their respective curcibles until the difference in initial and final weights was equal to the desired sample or reference size. In the case of diluted samples, a piece of clean filter paper was first weighed and then reference material was added until the desired amount of reference material was obtained. The reference material was then added to the sample crucible and intermixed with the sample material with a stainless steel spatula. The spatula, which was also used in depositing reference or sample material into the crucibles or onto the filter

paper, was cleaned in acetone previous to its use in any weighing so as to prevent contamination. The balance used in all sample and reference material weighings was a Mettler analytical balance accurate to ± 0.0005 milligrams.

A hard sample packing, as recommended in Chapter II was used in this study to aid reproducibility. A glass rod, cleaned in acetone and sized to closely fit the crucible diameter, was used to pack both sample and reference materials. A packing presure of approximately 4,000 grams per square centimeter was used in all tests.

Test Procedure

The steps involved in the actual experimental test procedure include (1) sample holder, and sample and reference crucible placement, (2) furnace position placement, (3) DTA sensitivity control, (4) TGA sensitivity control, (5) atmosphere control, (6) heating rate selection, and (7) calibration.

Sample Holder Placement. The sample holder was first plugged into its corresponding jack on the balance arm. The holder base was keyed so as to locate the holder in only one position. A heat source was applied to the reference junction of the differential thermocouple with the subsequent deflection of the recorder pen on the DTA channel being noted as indicating an endothermic response. The prepared reference and sample crucibles were then placed on their respective thermocouple junctions with tweezers, with which the crucibles were always handled. The crucibles were then firmly seated on the junctions to insure good electrical contact. To insure symmetric and uniform

heating of each crucible, the sample holder was made co-axial with the furnace center line with the jig which is supplied with the Mettler Thermoanalyzer 2 for this purpose. This device was used prior to each test.

At the completion of each test, the sample and reference crucibles were removed from the sample holder and thoroughly cleaned before reusing. The cleaning procedure consisted of a thorough rinsing with hydorchloric acid followed by a water rinse. The curcibles were then placed into a gas flame of approximately 1000°C until they became cherry red in color. This last step insured that there would be no reactible material left on the crucibles prior to the next experiment.

Furnace Position. The Mettler Mid-Range Furnace was a circular spiral wound furnace which had the capability of being rotated to any position around a 360° arc. The position most desired was the one which gave the least base-line drift as determined when identical reference and sample crucibles were heated. A series of tests at a heating rate of 25°C/minute using both empty crucibles and crucibles containing equal amounts of gold powder, was performed while the furnace position was varied. The furnace position, as indicated by the power input jack, which produced the least base-line drift, as shown by Figure 9 in Appendix B, was used in all subsequent tests.

DTA Sensitivity. The DTA sensitivity used in this study varied according to sample size and reaction of interest. Low DTA sensitivity made the task of distinguishing small heats of reaction impossible,

while a high DTA sensitivity made it very difficult to follow reactions accompanied by the liberation of large amounts of heat. A DTA sensitivity of 20 microvolts per inch was used with the Fisher Al_2O_3 and five microvolts per inch with the gold powder. The high DTA sensitivity proved necessary due to the small magnitude of the endothermic heat of decomposition sought by this study.

TGA Sensitivity. The TGA sensitivity was kept at the maximum value for both recording channels, namely 10 and one milligrams per inch for the general and expanded weight loss channels respectively. The maximum sensitivity was necessary due to the low sample weight used in this study.

Atmosphere Control. The dynamic atmosphere, as stated above, was supplied by a compressed air tank, obtained from Air Products, Inc., Chamblee, Georgia, through a two stage pressure regulator and a ball rotometer. The flowmeter was set to provide a flow rate of 12 millileters per minute of air through the furnace.

The air was allowed to flow through the furnace and past the sample crucibles for a period of approximately 15 minutes prior to the furnace turn-on. This pre-flow was necessary to purge the furnace of its previous atmosphere and to stabilize the weight loss base-line, which experienced an initial loss in weight prior to furnace turn-on.

Heating Rate Selection. It was desired that a heating rate be used in this study which would be sufficiently fast that the fabric response would be characteristic of its decomposition behavior when undergoing combustion. Each fabric was tested at heating rates of 25 and 10°C per minute, the former rate being the maximum obtainable

heating rate with the Mettler Thermoanalyzer 2.

Calibration. It was necessary to perform two types of calibration experiments on the Mettler Thermoanalyzer 2. As the furnace atmosphere is heated, the air density changes resulting in a change of buoyancy which causes an apparent weight gain. Calibration tests, shown in Figures 9 and 10 in Appendix B, were performed on amounts of reference material identical with the total amount of material used in the fabric tests. In the case of the gold powder reference, the furnace position tests doubled as the buoyancy calibration tests. The buoyancy change was evaluated as a function of time for each heating rate and then added to the recorded weight loss trace to obtain the true weight loss as a function of time.

The heat of reaction calibration constants were found by performing simultaneous DTA/TGA experiments on potassium nitrate (KNO_3). The heat of fusion of KNO_3 is known to be 28.1 calories per gram with a melting temperature of 338°C [56]. The KNO_3 calibration tests were performed at heating rates of 25 and 10°C per minute with 100 milligrams of gold powder in the reference crucible and 50 milligrams of gold powder and 50 milligrams of KNO_3 in the sample crucible. The DTA sensitivity was five microvolts per inch, the dynamic air flow rate was 12 millimeters per minute.

Analytical Procedure

The analytical procedure consists of the methods used in the evaluation of the kinetic parameters of n, E, and k_o and the reaction enthalph, ΔH, from the raw DTA/TGA data.

Reaction Parameter Evaluation

Three methods of kinetic parameter evaluation were used in this work called Methods I, II, and III as described below. Also described are the methods used in evaluating McCarter's data.

Method I. The basis of Method I involves forming the ratio of equations (1), written at any instant of time during the reaction, to equation (1) written for the instant of greatest sample weight change. Taking the natural logarithm and rearranging results in

$$\frac{\ln(\dot{x}/\dot{x}_m)}{\ln[(1-x)/(1-x_m)]} = n - \frac{E/R(1/T - 1/T_m)}{\ln[(1-x)/(1-x_m)]} \qquad (8)$$

Equation (8) yields a straight line of slope - E/R and intercept n when plotted for Arrhenius-type reactions. A computer program was coded to perform the above task so as to yield values n, E, and k_o.

Values of weight loss and temperature were read off the fabric thermogravimetric trace at evenly spaced intervals of time during a reaction. These values along with the number of data points, the time interval, and the total weight of fabric reacted were read into to computer program on data cards. The program evaluated x for each data point and, using a four point numerical differentiation method, evaluated $\dot{x}$ for each point. The program computes the values of the plotting variables $\ln(\dot{x}/\dot{x}_m)/\ln[(1-x)/(1-x_m)]$ and $(1/T - 1/T_m)/\ln[(1-x)/(1-x_m)]$ for each data point except $T = T_m$, which was evaluated as shown below. When $T = T_m$, the two plotting variables become indeterminate. L'Hospital's rule was applied this case to find the limiting values of

the plotting variables as $T \to T_m$. These were found to be

$$\lim_{T \to T_m} \frac{\ln(\dot{x}/\dot{x}_m)}{[(1-x)/(1-x_m)]} = -\frac{\ddot{x}_m(1-x_m)}{\dot{x}_m^2} \tag{9}$$

and

$$\lim_{T \to T_m} \frac{(1/T - 1/T_m)}{[(1-x)/(1-x_m)]} = \frac{\phi(1-x_m)}{T_m^2 \cdot \dot{x}_m} \tag{10}$$

A least-square fit line was computed through the coordinates of the plotting variables. The order of reaction and the activation energy were obtained from the intercept and the slope, -E/R, of the least square line. The pre-exponential factor was evaluated by solving equation (1) for k_o, and averaging the k_o's obatined from each data point. The measure of the least-square fit line was evaluated and reported as the square of the correlation coefficient which is described under Method III.

Method II. Method II was arrived at by first differentiating equation (1) to find the maximum rate of weight change, $\dot{x}_m$,

$$\dot{x}_m = [(1-x_m)/n] \, (E\phi/RT_m^2) \tag{11}$$

which was combined with equation (1) to yield

$$(1-x_m)^{1-n}/n = (k_o RT_m^2/ E\phi)e^{-E/RT} \tag{12}$$

Equation (1) was integrated and, making a partial integration of the

right side and neglecting small terms, became

$$\frac{(1-x)^{1-n} - 1}{n-1} \simeq (k_o RT_m^2/\phi E)e^{-E/RT_m} \quad , \tag{14}$$

which combined with equation (12), yielded

$$(1-x_m)^{1-n} \simeq n \qquad n \neq 1 \quad . \tag{15}$$

An expanded plot of $x(t)$, $\dot{x}(t)$, and $T(t)$ was made for each reaction of interest for which the values of T were obtained from the thermogravimetric trace while the values of x and $\dot{x}$ were those values returned from the computer program used in Method I.

From these expanded plots, the values of $\dot{x}_m$, x_m, and T_m were located and used in equations (15), (11), and (1) to evaluate n, E, and k_o respectively.

Method III. Method III eliminated the need to know the values of $\dot{x}(t)$ during a reaction, requiring a knowledge of $x(t)$ and $T(t)$ only. Equation (1) was integrated, with a partial integration of the right side being made and small terms neglected, and natural logarithms taken to yield

$$\ln\left\{\frac{[1-(1-x)^{1-n}]T_o^2}{(1-n)\,T^2}\right\} = \ln\left\{\frac{k_o RT_o^2}{\phi E}\right\} - \frac{E}{R}\frac{1}{T} \quad . \tag{16}$$

If the correct value of n is known, a plot of $\ln\{[1-(1-x)^{1-n}]T_o^2/(1-x)\,T^2\}$ versus $1/T$ yields a straight line of slope $-E/R$ from which the

activation energy is easily found. In this study n was unknown and was determined by finding that n which produced the optimum least-square fit line with the highest correlation coefficient squared through the plot corresponding to that n.

The general equation of a least-square line is

$$z = \bar{z} + b(y-\bar{y}) \tag{17}$$

where, in general the superscripted bar denotes the arithmetic mean:

$$\bar{u} = \frac{1}{N} \sum_{i=1}^{N} u_i \quad . \tag{18}$$

The correlation coefficient is defined as

$$r = b \frac{s_y}{s_z} \tag{19}$$

where b is the regression coefficient,

$$b = \frac{s_{yz}}{s_y^2} \quad , \tag{20}$$

and s_y, s_z, and s_{yz}, the standard deviations of y, z, and z on y respectively, are defined below. The correlation coefficient is a statistical tool used to indicate how well a group of points represent a straight line. The square of the correlation coefficient, B, is more frequently used and can only have a value between zero and one inclusive. A value near one indicates a high correlation while a value

near zero indicates a low correlation.

As stated above the value of n directly varies the value of the left side of equation (16) and so varies the correlation of the least-square line, making B a function of n. A new function of n was found such that

$$X(n) = B(n) - 1 \tag{21}$$

would be a minimum when the correct value of n was used in equation (16). It was assumed that the value of n which gave X(n) to be a minimum or dX/dn to be zero would be the correct value. Differentation of X(n) yields

$$\frac{dX}{dn} = \frac{dB}{dn} = 2B \left[\frac{\dot{s}_{yz}}{s_{yz}} - \frac{\dot{s}_z}{s_z} - \frac{\dot{s}_y}{s_y}\right] \tag{22}$$

where

$$s_{yz} = \frac{1}{N} \sum_{i=1}^{N} y_i z_i - \bar{y}\,\bar{z} \quad , \tag{23}$$

$$\dot{s}_{yz} = \frac{1}{N}\left[\sum_{i=1}^{N} y_i z_i - \bar{x} \sum_{i=1}^{N} \dot{z}_i\right] \tag{24}$$

$$s_y^2 = \frac{1}{N} \sum_{i=1}^{N} y_i^2 - \bar{y}^2 \tag{25}$$

$$\dot{s}_y = 0, \tag{26}$$

$$s_z^2 = \frac{1}{N} \sum_{i=1}^{N} z_i^2 - \bar{z}^2 \quad , \tag{27}$$

$$\dot{s}_z = \frac{1}{s_z N} \left[\sum_{i=1}^{N} z_i \dot{z}_i - \bar{z} \sum_{i=1}^{N} \dot{z}_i \right] \quad , \tag{28}$$

and

$$y_i = 1/T_i \quad , \tag{29}$$

$$z_i = \ln \left[\frac{(1 - (1-x_i)^{1-n}) \, T_o^2}{(1-x) \, T_i^2} \right] \tag{30}$$

$$\dot{z}_i = \frac{(1-x_i)^{1-n}[(1-n)\ln(1-x_i) - 1] + 1}{[1-(1-x_i)^{1-n}](1-n)} \tag{31}$$

A computer subroutine was added to the program introduced in Method I, and was designed to utilize the existing data cards containing the fabric thermogravimetric data. The subroutine was initially given 10 values of n for which it calculated the least-square lines and their corresponding X and $\dot{X}$ values. The program then searched for the value of n which caused a change in sign of $\dot{X}$. A Newton-Raphson method of iteration, as described below, was used to obtain that value of n which caused $\dot{X}$ to be zero.

In order to perform a Newton-Raphson iteration, it was necessary to obtain the second derivative of X, $\ddot{X}$. This was accomplished using a four point, numerical differentiation method. The actual iteration was

performed according to equation (32)

$$n_{j+1} = n_j - \frac{\dot{X}_j}{\ddot{X}_j} \tag{32}$$

That value of n which caused a change in sign of $\dot{X}$ was used to begin the iteration which was reported until $\dot{X}$ obtained a value of ±0.01.

At the end of the iteration procedure, the best least-square line was calculated along with its slope and intercept. With n known, E was evaluated from the slope of -E/R, while k_o was found from the intercept of $\ln[k_o R T_o^2/\phi E]$.

Reaction Parameter Evaluation of McCarter's Data. McCarter's data, as stated previously, yielded a direct measure of the rate of weight change as opposed to the fraction of weight reacted which was recorded in this study. Since McCarter claims that the area under his combustible gas curve is equivalent to the total weight of reacted fabric, a computer program was coded to read in McCarter's data as a function of time and to integrate the area under the curve as a function of time by a Simpson integration method. The actual rate of change of weight fraction, $\dot{x}(t)$, is found by dividing the signal read from McCarter's data by the total area under the curve. The weight fraction reacted, x(t) is found by dividing the area under the curve as a function of time by the total area under the curve.

With a knowledge of $\dot{x}(t)$ and x(t) from the computer program and T(t) from McCarter's data, Method I was employed to evaluate n, E, and k_o from the data of McCarter on nine of the ten fabrics studied in this

work. Expanded curves of $\dot{x}(t)$, $x(t)$, and $T(t)$ were also made for McCarter's data and the value of weight fraction, x_m, corresponding to the maximum rate of weight change, $\dot{x}_m$, was read off and used in Method II to evaluate n and E, while k_o was found from equation (1). As before, the correlation coefficient squared, B, for the least-square fit line of Method I was evaluated.

Reaction Enthaply Evaluation

Although it has been shown previously that equation (3) has been used to measure the enthalpy of pyrolysis of fabrics, it was felt that this method did not take into consideration changes in heat capacity of the sample due to mass loss of the sample. A new method, developed by Dr. Wolfgang Wulff, was used in the reaction enthalpy determination which has its basis in the comparison of the conservation of energy equations for a melting substance of known heat of fusion and for a fabric sample of unknown heat of reaction, while taking into account changes in heat capacity of the materials.

Calibration Sample. The calibration tests performed on potassium nitrate (KNO_3), as previously mentioned, are shown in Figures 7 and 8, in which the larger endothermal peaks correspond to the melting of the KNO_3. The conservation of energy equations for the sample crucible with KNO_3 present and the reference crucible are first written. For the sample crucible

$$C_s dT_s = - dH + K(T_f - T_s)dt \qquad (33)$$

where K is the overall heat transfer coefficient and C_s represents the

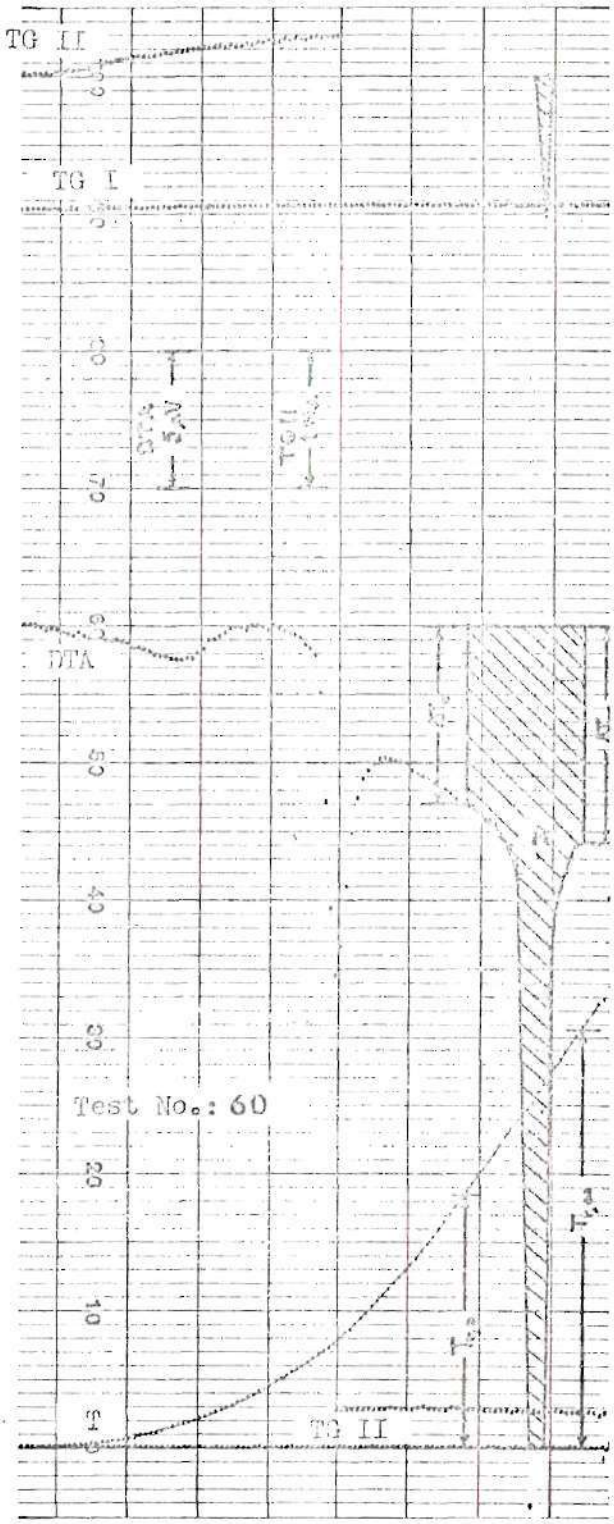


Figure 7. DTA Thermogram of KNO_3 Reaction Enthalpy Calibration Test at a Heating Rate of 25°C per minute. (Linear Reduction=71%)

Figure 8. DTA Thermogram of KNO_3 Reaction Enthalpy Calibration Test at a Heating Rate of 10°C per minute. (Linear Reduction=63%)

heat capacity of the sample crucible and its contents as given by equation (34)

$$C_s = m_{c,s}\ c_c + m_{g,s}\ c_g + m_{KNO_3}\ c_{KNO_3} \tag{34}$$

where $m_{c,s}$ and $m_{g,s}$ are the masses of the sample crucible and the gold powder diluent respectively. For the reference crucible

$$C_r dT_r = K(T_f - T_r)\ dt \tag{35}$$

where

$$C_r = m_{c,r}\ c_c + m_{g,r}\ c_g \tag{36}$$

and K is assumed to be identical for both crucibles. Equation (36) is substracted from equation (34) and the result integrated from t=0 to t=∞ to obtain

$$H_{KNO_3} = C_s(\Delta T_o - \Delta T_\infty) - KA + \varepsilon C_s(T_{r,\infty} - T_{r,o}) \tag{37}$$

where A is the area under the DTA thermogram and $\varepsilon = C_r/C_s - 1$. Equation (37) was used to calculate K using appropriate values found from the KNO_3 tests in Figures 7 and 8 recorded in Table 2. An average value of K for the two heating rates was found to be 0.00782 cal./sec. °K.

Fabric Sample. The conservation of energy equations are written for the fabric sample experiencing a mass loss. For the sample crucible

$$(C_{so} + w\ c)\ dT_x = -\ dH + K(T_f - T_s)dt \tag{38}$$

Table 2. KNO_3 Parameters Used in Evaluation of Overall Heat Transfer Coefficient*.

$m_{c,s}$	=	1.025 g.	
$m_{c,r}$	=	1.037 g.	
c_c	=	0.0328 cal./g °K	
c_g	=	0.0316 cal./g. °K	Found in Reference [60].
c_{KNO_3}	=	0.228 cal./g. °K	
ΔH_{KNO_3}	=	28.1 cal./g.	
Test No.: 60			
ϕ	=	25 °C/min.	
m_{KNO_3}	=	0.0504 g.	
$m_{g,s}$	=	0.0489 g.	
$m_{g,r}$	=	0.0979 g.	
C_s	=	0.0470 cal./°C	
ε	=	-0.202	
A	=	-345 sec.-°C	
$\Delta T_o - \Delta T_\infty$	=	0.15 °C	
$T_{r,\infty} - T_{r,o}$	=	129 °C	
Test No.: 72			
ϕ	=	10 °C/min.	
m_{KNO_3}	=	0.0500 g.	
$m_{g,s}$	=	0.0489 g.	

*Physical properties evaluated at a mean temperature of 300°C.

Table 2. (Continued)

$m_{g,r}$	=	0.0984 g.
C_s	=	0.0470 cal./°C
ε	=	=-.202
A	=	227 sec.-°C
$\Delta T_o - \Delta T_\infty$	=	-0.14 °C
$T_{r,\infty} - T_{r,o}$	=	52 °C

---

where w and c are the mass of reacting fabric as a function of time and its specific heat respectively and C_{so} is the heat capacity of the sample crucible and its contents, except for that part of the fabric which reacts, as given by equation (39)

$$C_{so} = m_{c,s}\, c_c + m_{g,s}\, c_g + (m_o - w_\infty)\, c \tag{39}$$

where m_o is the initial fabric mass and w_∞ is the total mass of reacted fabric. For the reference crucible

$$C_r dT_r = K(T_f - T_r)\, dt \tag{40}$$

where

$$C_r = m_{c,r}\, c_c + m_g\, c_g \tag{41}$$

as before. Equation (40) is subtracted from equation (38) and integrated from t = o to t = ∞ to yield

$$H_{fabric} = C_{so}(\Delta T_o - \Delta T_\infty) - KA + \varepsilon' C_{so}(T_{r,\infty} - T_{r,o}) - c \int_o^\infty w dT_s \quad (42)$$

where $\varepsilon' = C_r/C_{so} - 1$ and K is assumed to be the same as was calculated previously for the KNO_3 sample.

The last term in equation (42) may be simplified by way of the following substitution,

$$\int_o^\infty w dT_s = \int_o^\infty wd(T_r+\Delta T) = \phi \int_o^\infty wdt + \int_{\Delta T_o}^{\Delta T_\infty} wd(\Delta T) \quad . \quad (43)$$

The ratio of equation (42) and (37) is now made, noting the simplification of equation (43) and noting that $\Delta H_f = H_{fabric}/m_o$ with units of calories per gram of initial fabric mass.

$$\Delta H_{fabric} = \left(\frac{\Delta H_{KNO_3} \cdot m_{KNO_3}}{m_o} \right) \cdot \frac{H_{fabric}}{H_{KNO_3}} \quad . \quad (44)$$

A computer program was coded to read in the values of fabric mass, differential temperature, and temperature at a number of evenly spaced time intervals. In addition the values of specific heat, mass of reference material, mass of diluent, number of data points, and time interval were also read in. For each fabric, the computer evaluated C_{so} and ε' while a subroutine evaluated the three integrals in the numerator of equation (44) with a Simpson integration method.

The remaining parameters needed to evaluate equation (44) were supplied to the program itself. The values of fabric specific heat, c, are tabulated in Appendix A.

Thermoplastic Fabrics. The heat of fusion of the melting GIRCFF fabrics was evaluated with a modified version of equation (44). Neglecting small terms, equation (44) reduces to

$$\Delta H_{fabric} = \frac{(\Delta H_{KNO_3} \cdot m_{KNO_3}) \cdot A_{fabric}}{m_o \cdot A_{KNO_3}} \qquad (45)$$

A computer program was coded to incorporate equation (45) by which initial fabric mass and the fabric's differential temperature at a number of evenly spaced time intervals were read in on data cards. The area, A, was evaluated with a Simpson integration method while the remaining parameters in equation (45) were written into the program. The program returned both the heat of fusion and the integrated area under the DTA curve.

CHAPTER V

RESULTS

The chapter on results is divided into the section on kinetic parameter results and reaction enthalpy results, plus the section listing the kinetic parameters evaluated from McCarter's data. The actual DTA/TGA thermograms of the GIRCFF fabrics are found in Appendix B along with a listing of the experimental conditions employed in each test.

Kinetic Parameter Results

The results of the kinetic parameter evaluations for the endothermal decomposition of the GIRCFF fabrics are found in Tables 3, 4, and 5 according to the method of analysis used. The results of the kinetic parameter evaluations for the exothermal decomposition of the GIRCFF fabrics are found in Tables 6 and 7. The least-square lines used in evaluating the kinetic parameters for the endothermal decomposition by Methods I and III are found in Appendix C.

Reaction Enthalpy Results

The results of the enthalpy of decomposition and the heat of fusion evaluations for the GIRCFF fabrics are found in Tables 8 and 9 respectively.

Kinetic Parameter Results from McCarter's Data

The kinetic parameter results evaluated from Dr. McCarter's data on the GIRCFF fabrics is listed in Tables 10 and 11 according to

the method of analysis. The least-square lines used to evaluate the kinetic parameters by Method I are found in Appendix C.

Table 3. Kinetic Parameters for Endothermal Decomposition of GIRCFF Fabrics in Dynamic Air Atmosphere Evaluated by Method I.

GIRCFF Fabric No.	Heating Rate (^{o}C/Min.)	Temp. Range (^{o}C)	$\frac{W_{\infty}}{m_{o}}$ (%)	Order of Reaction	Activation Energy (kcal./mole)	Pre-exponential Factor (1/sec.)	B
5	25	28-146	4.28	2.5	24.4	2.73×10^{14}	0.958
5	10	36-120	1.85	2.1	23.4	1.00×10^{13}	0.973
10	25	28-169	3.05	2.4	20.0	1.26×10^{11}	0.982
10	10	25-120	4.04	2.2	20.7	5.55×10^{11}	0.964
18	25	31-140	2.87	2.2	23.9	5.68×10^{13}	0.977
18	10	30-103	2.35	2.4	33.4	6.43×10^{20}	0.954
19	25	28-120	2.52	2.1	23.0	2.52×10^{13}	0.955
19	10	35-90	1.29	2.0	30.8	4.86×10^{18}	0.951
11	25	28-94	2.24	2.2	28.8	6.72×10^{17}	0.976

Table 4. Kinetic Parameters for Endothermal Decomposition of GIRCFF Fabrics in Dynamic Air Atmosphere Evaluated by Method II.

GIRCFF Fabric No.	Heating Rate (^{o}C/min.)	$\frac{W_\infty}{m_o}$ (%)	$\dot{x}_m$ (1/sec) x 10^{-3}	x_m	T_m (^{o}C)	Order of Reaction	Activation Energy (kcal./mole)	Pre-exponential Factor (1/sec.)
5	25	4.28	3.50	0.47	58	2.3	22.4	7.87×10^{10}
5	10	1.85	2.84	0.53	71	1.7	24.2	1.35×10^{11}
10	25	3.05	3.50	0.49	67	2.1	22.2	2.48×10^{10}
10	10	4.04	2.00	0.48	56	2.2	18.4	8.55×10^{7}
18	25	2.87	5.00	0.54	68	1.6	30.7	1.54×10^{15}
18	10	2.35	2.50	0.54	52	1.6	18.6	5.87×10^{8}
19	25	2.52	3.67	0.52	60	1.8	16.5	2.64×10^{7}
19	10	1.29	3.17	0.58	56	1.3	19.9	2.14×10^{9}
11	25	2.24	4.34	0.52	50	1.8	20.2	9.65×10^{9}

Table 5. Kinetic Parameters for Endothermal Decomposition of GIRCFF Fabrics in Dynamic Air Atmosphere Evaluated by Method III.

GIRCFF Fabric No.	Heating Rate (^{o}C/min.)	Temp. Range (^{o}C)	$\frac{W_{\infty}}{\overline{m}_{o}}$ (%)	Order of Reaction	Activation Energy (kcal./mole)	Pre-exponential Factor (1/sec.)	B
5	25	28-146	4.28	2.6	23.3	4.88×10^{13}	0.994
5	10	36-120	1.85	2.3	25.4	2.12×10^{14}	0.993
10	25	28-169	3.05	2.9	21.4	1.77×10^{12}	0.992
10	10	25-120	4.04	2.2	21.2	1.00×10^{12}	0.985
18	25	31-140	2.87	2.5	25.1	4.74×10^{14}	0.993
18	10	30-103	2.35	2.3	30.4	3.40×10^{18}	0.981
19	25	28-120	2.52	2.3	24.3	2.00×10^{14}	0.991
19	10	35-90	1.29	3.3	48.2	7.70×10^{10}	0.989
11	25	28-94	2.24	2.9	36.1	1.28×10^{23}	0.994

Table 6. Kinetic Parameters for Exothermal Decomposition of GIRCFF Fabrics in Dynamic Air Atmosphere Evaluated by Method I.

GIRCFF Fabric No.	Heating Rate (°C/min.)	Temp. Range (°C)	$\frac{w_\infty}{m_o}$ (%)	Order of Reaction	Activation Energy (kcal./mole)	Pre-exponential Factor (1/sec.)	B
2	25	337-490	95.4	2.1	67.9	2.30×10^{19}	0.914
2	10	333-477	95.8	1.6	70.6	2.01×10^{20}	0.969
5	25	248-392	90.9	2.8	53.6	1.26×10^{18}	0.796
5	10	240-394	90.0	3.2	50.2	2.09×10^{16}	0.621
8	25	240-411	93.3	4.7	41.0	3.24×10^{12}	0.829
10	10	178-579	91.6	2.5	24.4	5.60×10^{6}	0.985
10	10	191-416	91.4	0.9	30.2	3.95×10^{8}	0.878
11	25	256-426	90.6	3.6	56.8	2.89×10^{18}	0.553
11	10	249-392	86.9	3.9	53.6	2.58×10^{17}	0.554
12	10	235-505	93.0	2.1	29.2	9.50×10^{6}	0.461

Table 6. (Continued)

GIRCFF FABRIC No.	Heating Rate (°C/min.)	Temp. Range (°C)	$\frac{W_\infty}{m_o}$ (%)	Order of Reaction	Activation Energy (kcal./mole)	Pre-exponential Factor (1/sec.)	B
13	25	253-425	94.9	2.6	55.0	9.49×10^{17}	0.855
13	10	246-433	91.4	1.5	47.4	6.07×10^{14}	0.901
17	25	240-415	99.3	6.2	36.7	7.19×10^{10}	0.918
17	10	224-380	94.7	2.6	36.6	3.58×10^{10}	0.987
18	25	238-408	90.4	2.5	55.8	4.87×10^{18}	0.730
18	10	245-349	90.9	2.8	79.8	5.17×10^{27}	0.695
19	25	202-389	88.4	3.9	34.6	1.43×10^{11}	0.872
19	10	166-376	87.7	4.7	32.8	2.82×10^{10}	0.562

Table 7. Kinetic Parameters for Exothermal Decomposition of GIRCFF Fabrics in Dynamic Air Atmosphere Evaluated by Method III.

GIRCFF Fabric No.	Heating Rate (^{o}C/min.)	Temp. Range (^{o}C)	$\frac{W_{\infty}}{m_{o}}$ (%)	Order of Reaction	Activation Energy (kcal./mole)	Pre-exponential Factor (1/sec.)	B
2	25	337-490	95.4	0.8	48.7	9.81×10^{12}	0.980
2	10	333-477	95.8	1.2	54.4	8.35×10^{14}	0.964
5	25	248-392	90.9	1.5	35.8	1.26×10^{11}	0.955
5	10	240-394	90.0	1.6	34.1	9.20×10^{9}	0.976
8	25	240-411	93.3	1.8	30.7	3.12×10^{8}	0.986
10	25	178-579	91.6	3.2	28.6	2.52×10^{8}	0.985
10	10	191-416	91.4	1.0	22.6	3.30×10^{5}	0.966
11	25	256-426	90.6	1.4	31.3	6.97×10^{8}	0.941
11	10	249-392	86.9	1.0	29.3	8.63×10^{7}	0.966
12	10	235-505	93.0	0.1	18.8	9.78×10^{2}	0.983

Table 7. (Continued)

GIRCFF Fabric No.	Heating Rate (°C/min.)	Temp. Range (°C)	$\frac{W_\infty}{m_o}$ (%)	Order of Reaction	Activation Energy (kcal./mole)	Pre-exponential Factor (1/sec.)	B
13	25	253-425	94.9	1.4	32.7	3.08×10^{9}	0.937
13	10	246-433	91.4	2.0	33.7	5.88×10^{9}	0.904
17	25	240-415	99.3	3.0	25.2	2.67×10^{6}	0.986
17	10	224-380	94.7	2.0	25.9	2.86×10^{6}	0.994
18	25	238-408	90.4	1.2	37.3	2.20×10^{11}	0.956
18	10	245-349	90.9	0.5	44.0	5.89×10^{13}	0.944
19	25	202-389	88.4	1.8	22.0	8.60×10^{5}	0.957
19	10	166-376	87.8	0.8	20.4	7.79×10^{4}	0.973

Table 8. Reaction Enthalpies for Endothermal Decomposition of GIRCFF Fabrics in Dynamic Air Atmosphere.

GIRCFF Fabric No.	Heating Rate (°C/min.)	Temperature Range (°C)	$\frac{W_\infty}{m_o}$ (%)	Enthalpy of Reaction (cal./g.)
5	10	36-120	1.85	40.2
10	10	25-120	1.85	40.2
18	25	31-140	2.87	17.7
18	10	30-103	2.35	38.1
19	25	28-120	2.52	66.1
19	10	35-90	1.29	32.2
11	25	28-94	2.24	25.7

Table 9. Heats of Fusion of Thermoplastic GIRCFF Fabrics and Blends Undergoing Melting in Dynamic Air Atmosphere.

GIRCFF Fabric No.	Heating Rate (°C/min.)	Temperature Range (°C)	Melting Temperature (°C)	Heat of Fusion (cal./g.)
2	25	194-307	252	22.2
8	25	199-280	242	10.5
11	25	210-288	245	20.0
12	25	225-357	283	23.4
17	25	225-272	240	6.8

Table 10. Kinetic Parameters Evaluated from McCarter's Data [48] on GIRCFF Fabrics Decomposing in Dynamic Nitrogen Atmosphere by Method I.

GIRCFF Fabric No.	Heating Rate (°C/min.)	Temp. Range (°C)	$\frac{W_\infty}{m_o}$ (%)	Order of Reaction	Activation Energy (kcal./mole)	Pre-exponential Factor (1/sec.)	B
2	60	414-529	96.0	1.7	87.0	1.04×10^{24}	0.983
5	60	324-466	91.0	1.4	71.0	3.07×10^{21}	0.995
10	60	319-478	87.5	1.2	56.6	3.38×10^{16}	0.995
11	60	350-457	100.0	2.9	123.0	6.71×10^{38}	0.989
12	60	404-535	100.0	2.1	118.5	1.65×10^{33}	0.987
13	60	360-476	98.0	2.4	128.8	7.56×10^{40}	0.935
17	60	348-443	90.2	2.1	87.4	1.28×10^{27}	0.994
18	60	333-478	90.4	1.6	81.3	7.26×10^{24}	0.992
19	60	319-396	55.8	2.1	144.4	5.33×10^{49}	0.978

Table 11. Kinetic Parameters Evaluated for McCarter's Data [48] on GIRCFF Fabrics Decomposing in Dynamic Nitrogen Atmosphere by Method II.

GIRCFF Fabric No. N	Heating Rate (^{o}C/min.)	$\frac{w_{\infty}}{m_{o}}$ (%)	$\dot{x}_m$	X_m	T_m	Order of Reaction	Activation Energy (kcal./mole)	Pre-exponential Factor (1/sec.)
2	60	96.0	2.05	0.59	487	1.2	71.7	3.15×10^{16}
5	60	91.0	1.93	0.61	417	1.1	52.5	9.54×10^{12}
10	60	87.5	1.97	0.61	425	1.1	54.6	2.85×10^{13}
11	60	100.0	2.50	0.44	407	2.7	112.3	1.06×10^{30}
12	60	100.0	2.80	0.60	473	1.2	92.1	8.33×10^{21}
13	60	98.0	2.62	0.59	409	1.2	73.7	1.20×10^{19}
17	60	90.2	2.27	0.54	409	1.6	74.2	1.80×10^{19}
18	60	90.4	1.93	0.60	420	1.2	54.9	4.98×10^{13}
19	60	55.8	4.64	0.47	354	2.3	159.7	7.90×10^{46}

CHAPTER VI

DISCUSSION OF RESULTS

The results of the kinetic parameter evaluation, the reaction enthalpy evaluation, and the kinetic parameter evaluation from McCarter's data are discussed in this chapter.

Discussion of Kinetic Parameter Results

Endothermal Decomposition

All of the GIRCFF fabrics, except GIRCFF Fabric No. 2, exhibited an endothermal decomposition reaction in the temperature range of 25 to 140 °C as shown in Figures 11 through 23 in Appendix B. These endothermal reactions were attributed to the desorption of moisture from the fabrics. Kinetic parameters were evaluated for only those DTA/TGA tests for which the loss of sample weight was greater than the noise of the balance signal. Only nine of the twenty DTA/TGA tests on the GIRCFF fabric with the gold powder reference resulted in a mass loss sufficient to evaluate the kinetic parameters for moisture desorption, those tests and their results being listed in Tables 3, 4, and 5.

When the mass fraction of sample at the end of moisture desorption was compared with reported regain values for cotton, nylon, acetate, and polyester, a large disparity was found to exist in that the reported regain values predicted considerably greater mass loss due to moisture desorption than was experienced. In the case of the cotton fabrics, the maximum mass loss was approximately four percent as opposed

to a reported regain value of nine percent [57], while the nylon and acetate fabrics experienced a mass loss of less than 1%, in general, as opposed to reported regain values of 4.5 percent and 6.5 percent respectively [58]. Only polyester, with its low value of regain, 0.4 percent [58], produced consistent moisture desorption data.

The reason for the contrast between the actual mass of moisture desorbed and that predicted by the regain values appears to be due to the fact that the dynamic atmosphere supplied by the compressed air tank was not at 65 percent relative humidity, but at a much lower value. During the time in which the weight loss base line was stabilizing, moisture from the fabric samples which were at 65 percent relative humidity, was evaporating into the dynamic atmosphere. Tests were initiated only after the weight loss was stabilized in order that there would be no change in weight at room temperature.

The results listed in Tables 3, 4, and 5 are consistent with each other, in general, regardless of method of analysis. The order of reaction appears to be high for most fabrics which may be due in part to the non-linearity of the temperature profile as may be seen in the figures in Appendix B. This non-linearity of the temperature is expecially noticeable at the 25°C per minute heating rate. As stated in Chapter II, a non-linear temperature rate may cause erroneous TGA and DTA results. The activation energy of GIRCFF No. 19, treated cotton, appears to be more heating rate dependent than the other fabrics, possibly due to the presence of the fire retardant which McCarter [48] reports to be of the alkaline-type.

Of the three methods of analysis, the highest confidence may be placed on Method III because there are more data points used than in Method II, and it does not require differentiation, as does Method I. The higher values of B also point to Method III as yielding the more reliable results.

Exothermal Decomposition

The kinetic parameter results for the GIRCFF fabrics, listed in Tables 6 and 7, are generally consistent with the reaction parameters listed in Table 1. A direct comparison between the exothermal results and the decomposition parameters evaluated in the literature from tests run in an inert atmosphere is not possible due to the higher complexity of the overlapping decomposition - oxidation reactions experienced in this study. The cotton fabrics, however, are consistant with results in Table 1, and the treated cotton does show a lower activation energy than the untreated cottons. GIRCFF Fabric No. 12, nylon, was not consistent with the results listed in Table 1, and this difference may be due in part to the difference in type of nylon used in each study.

Method III with its higher values of B and its lack of differentiation provides the more accurate and consistent values of kinetic parameters. Method I does not lend itself well to the evaluation of the exothermal parameters as indicated by the low B values.

Results from McCarter's Data

The results of the evaluation of kinetic parameters from McCarter's data may be compared with the exothermal decomposition results only qualitatively due to the difference in dynamic atmosphere for each

study. The results from McCarter's data may be compared quantatively with those of Table 1, although heating rate differences must be taken into account. The results from McCarter's, data expecially for the cottons and polyester, compare faborably with previous results. The results for the treated cotton and the thermoplastics and their blends do not compare favorably with previous works.

The treated cotton fabric, GIRCFF Fabric No. 19, yielded a much larger activation energy than was expected. This difference may be explained by the complications in treating the small initial reaction, which McCarter [48] states as representing the removal of hydroxyl groups from the cellulose substrate, and which precedes the major decomposition reaction. The fabric samples composed of blends of nylon, polyester, acetate, and cotton, namely GIRCFF Fabric Nos. 8, 11, and 17, produced inconsistent results due to the inability to correctly analyze McCarter's data which is characterized by two overlapping peaks on the combustible gas plot for each blend material.

Method II yields results more consistent with the values in Table 1 although more confidence can be placed on Method I since it utilized a large number of data points as opposed to the one point of Method II.

Discussion of Reaction Enthalpy Results

One intended result of this study was the evaluation of the endothermal heat of pyrolysis occuring prior to oxidation. No endothermal reaction was recorded in the temperature range expected. It was felt that the high heating rates used in this study caused the

exothermal heat of combustion to completely mask the endothermal heat of decomposition. The endothermal heat of moisture desorption was, however, evaluated as was the endothermal heat of fusion of the thermoplastic fabrics and their blends. The exothermal heat of combustion was not sought in this study and consequently was not evaluated.

Heat of Moisture Desorption

The heat of moisture desorption was evaluated for those nine DTA/TGA tests on GIRCFF Fabric Nos. 5, 10, 18, 19, and 11, for which there was a significant loss in weight due to moisture desorption as listed in Table 8. Of these nine tests, the tests on GIRCFF Fabric Nos. 5 and 10 at the heating rate of 25°C per minute were not evaluated due to excessive DTA base-line drift. The base-line drift of the other seven DTA tests due to the necessarily high heating rates also resulted in low confidence of the calculated heats of moisture desorption.

Heat of Fusion

The heats of fusion of the thermoplastic fabrics and their blends evaluated from the DTA tests at a heating rate of 25°C per minute compare well with the reported values of heat of fusion for melting fabrics. The values of heat of fusion of nylon and polyester compare especially well to the reported values of 22 calories per gram [58] and 20.3 calories per gram for nylon 6.6 [59], and 11 to 16 calories per gram for polyester [58].

The values of melting temperature for the melting GIRCFF fabrics also compare well to those reported previously [22]. It also appears that GIRCFF Fabric no. 12, nylon, and GIRCFF Fabric no. 11, nylon-

acetate blend, are composed on nylon 6.6 fibers, since the melting temperatures found for these fabrics is closer to that of nylon 6.6 than to that of nylon 6.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The results of the DTA/TGA tests on the GIRCFF fabrics were generally consistent with previous studies on textile materials as listed in Chapter II.

Kinetic Parameters

The kinetic parameters for moisture desorption from an untreated fabric are generally the same regardless of fabric type, heating rate, or amount of absorbed moisture. The desorption of moisture appears to be of order of reaction 2.5, activation energy 26 kcal. per mole, and pre-exponential factor 10^{14} $sec.^{-1}$.

The kinetic parameter evaluation for the exothermal reaction of the GIRCFF fabrics leads to less reliable results due to the complexity of the overlapping decomposition and oxidation reactions. The kinetic parameters results are especially influenced by method of analysis, more so than the evaluation of the kinetic parameters for the moisture desorption reaction.

Enthalpy of Reaction

The heat of moisture desorption is especially influenced by the fabric type, heating rate, and amount of water desorbed. The great amount of base-line drift resulting from the high heating rates used in this study limit the confidence of the evaluated heats of moisture

desorption to approximately ± 25 percent.

The heats of fusion evaluated from this study for nylon, polyester, and blends of these fabrics may be considered more reliable due to a lower base-line drift in the temperature range of interest for the melting fabrics. DTA does provide a reasonable method of evaluating the heats of fusion and melting temperatures of melting fabrics.

The endothermal pyrolysis reaction which was expected prior to combustion, and which did not appear, is felt to have been masked out by the exothermal reaction due to the high heating rates used in this study.

Recommendations

Future researchers should work to reduce the base-line drift experienced in the DTA tests. Further effort should be expended in finding a more suitable reference material with a specific heat closer to that of the fabric, but one which still experiences no moisture loss. A more even balance between heat capacity of the sample and reference crucibles would go far in reducing base-line drift.

Future researchers might also find it helpful to reduce the heating rate to a more practical value while the use of an inert atmosphere such as nitrogen, would help to seperate and identify the decomposition-oxidation reactions. Further investigation into sample preparation and the development of a more uniform packing procedure would also help to eliminate base-line drift.

Future studies should include the use of a recording facility which would maintain a separate recording channel and pen for each

signal so as to record a continuous signal. This would be very helpful in following fast moving reactions such as oxidation and fusion reactions.

APPENDIX A

GIRCFF FABRIC DESCRIPTION

The ten GIRCFF fabrics tested in this study are listed and described as to fabric type in Table 12 along with the values of specific heat used in the reaction enthalpy evaluations.

Table 12. GIRCFF Fabric Description.

GIRCFF Fabric No.	Fabric Description	Fiber Composition	Color	Specific Heat* (cal./g.-^{o}K)
2	Textured Woven Blouse	100% Polyester	Yellow	0.3394
5	T-shirt, Jersey	100% Cotton	White	0.4039
8	T-shirt, Jersey	65/35% Polyester/Cotton	White	0.3633
10	Batiste	100% Cotton	Purple	0.4637
11	Tricot	80/20% Acetate/Nylon	White	0.3466
12	Tricot	100% Nylon	White	0.5378
13	Tricot	100% Acetate	White	0.4015
17	Batiste	65/35% Polyester/Cotton	White	0.3442
18	Flannel	100% Cotton	White	0.3824
19**	Flannel	100% Cotton	White	0.3752

* Reprinted from Table II - 3 of Reference [5].

** Treated with fire retardant finish.

APPENDIX B

DTA/TGA TEST RUNS

The actual DTA/TGA thermograms of the GIRCFF fabrics used in the evaluation of the kinetic parameter and reaction enthalpy results are shown in Figures 9 through 23. Preceding each DTA/TGA thermogram is a data sheet containing the pertinent experimental parameters for each test.

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/1/72 TEST NO.: 59

SAMPLE MATERIAL : Gold Powder

SAMPLE AMOUNT : 99.3 Mg.

DILUENT MATERIAL : None

DILUENT AMOUNT : _____ Mg.

REFERENCE MATERIAL : Gold Powder

REFERENCE AMOUNT : 99.8 Mg.

THERMOCOUPLE : Pt / Pt - Rh 10 %

HEATING RATE : 25 °C / Min.

TEMPERATURE LIMITS : 25 TO 700 °C

GASEOUS ATMOSPHERE : Air

FLOW RATE : 12 Ml. / Min.

CHART PAPER FEED RATE : 12 Inch / Hr.

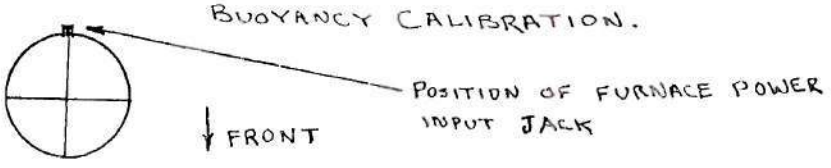
DTA SENSITIVITY : 5 μV / Inch

TG I SENSITIVITY : 10 Mg. / Inch

TG II SENSITIVITY : 1 Mg. / Inch

TEST INITIATION TIME : 11:05

REMARKS : Furnace Position and Atmosphere Buoyancy Calibration.



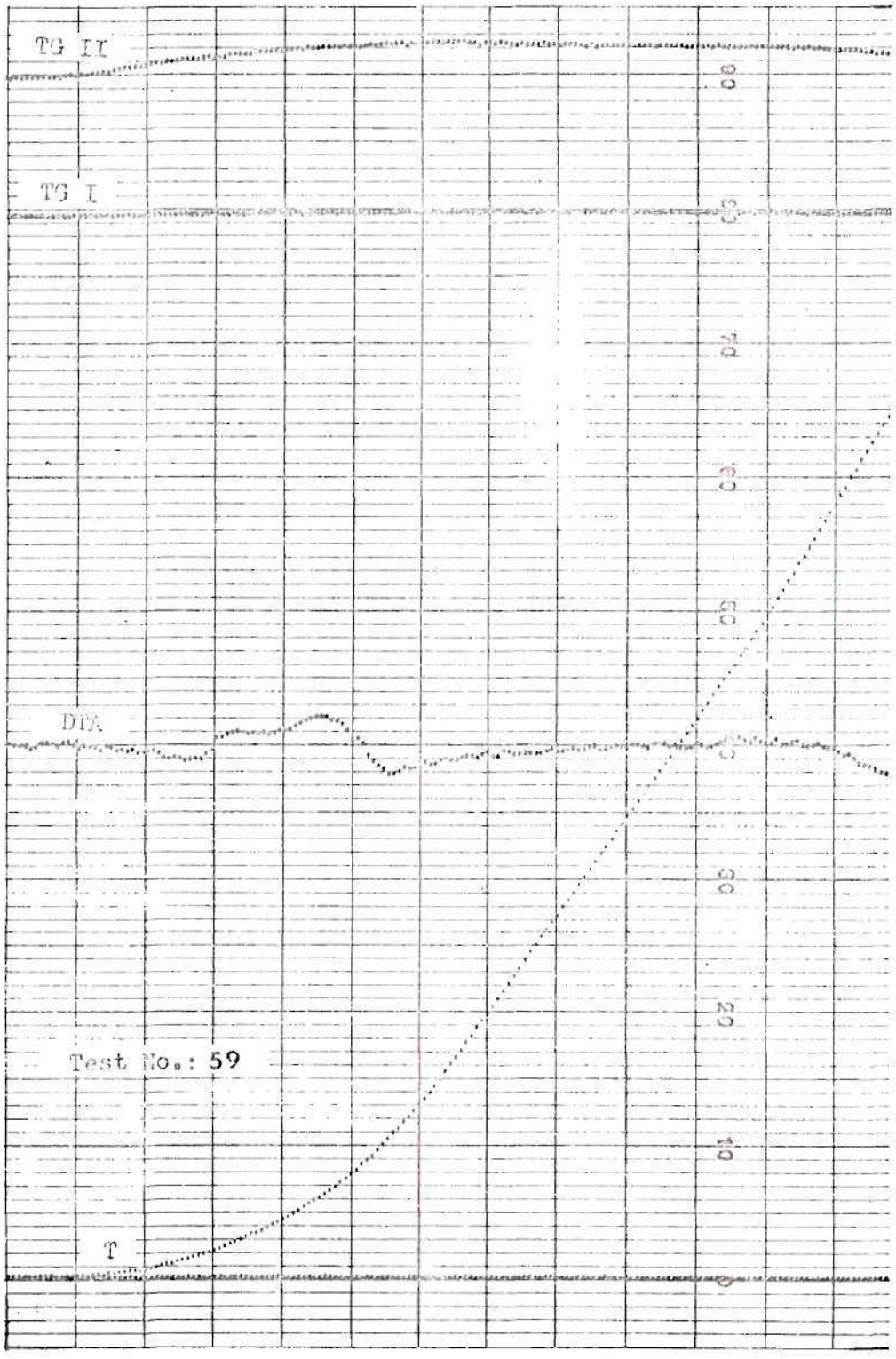


Figure 9. Selection of Optimum Furnace Position and Calibration of Buoyancy, DTA/TGA Test at Ø=25°C/min. (Linear Reduction=78%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/10/72 TEST NO.: 84

SAMPLE MATERIAL : Gold Powder

SAMPLE AMOUNT : 100.1 Mg.

DILUENT MATERIAL : None

DILUENT AMOUNT : _____ Mg.

REFERENCE MATERIAL : Gold Powder

REFERENCE AMOUNT : 99.8 Mg.

THERMOCOUPLE : Pt / Pt - Rh 10 %

HEATING RATE : 10 °C / Min.

TEMPERATURE LIMITS : 25 to 720 °C

GASEOUS ATMOSPHERE : Air

FLOW RATE : 12 Ml. / Min.

CHART PAPER FEED RATE : 12 Inch / Hr.

DTA SENSITIVITY : 5 μV / Inch

TG I SENSITIVITY : 10 Mg. / Inch

TG II SENSITIVITY : 1 Mg. / Inch

TEST INITIATION TIME : 10:40

REMARKS : Atmosphere Buoyancy Calibration

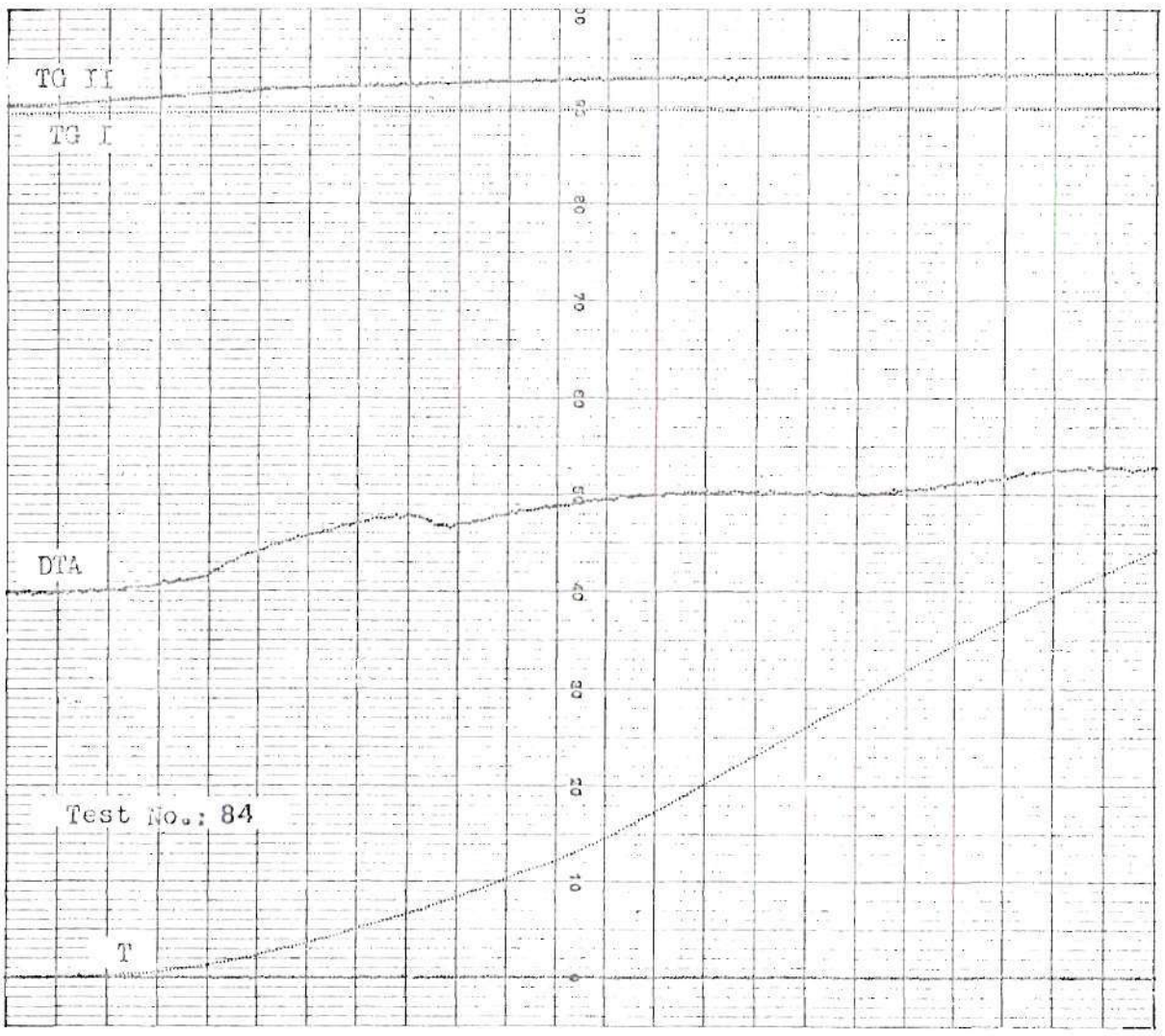


Figure 10. Buoyancy Calibration DTA/TGA Test at $\emptyset$=10°C/min. (Linear Reduction=52%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/3/72 TEST NO.: 65

SAMPLE MATERIAL: GIRCEE NO. 2

SAMPLE AMOUNT: 20.0 Mg.

DILUENT MATERIAL: GOLD POWDER

DILUENT AMOUNT: 79.6 Mg.

REFERENCE MATERIAL: GOLD POWDER

REFERENCE AMOUNT: 99.9 Mg.

THERMOCOUPLE: Pt / Pt - Rh 10 %

HEATING RATE: 25 °C / Min.

TEMPERATURE LIMITS: 25 TO 740 °C

GASEOUS ATMOSPHERE: AIR

FLOW RATE: 12 Ml. / Min.

CHART PAPER FEED RATE: 12 Inch / Hr.

DTA SENSITIVITY: 5 μV / Inch

TG I SENSITIVITY: 10 Mg. / Inch

TG II SENSITIVITY: 1 Mg. / Inch

TEST INITIATION TIME: 10:05

REMARKS: _____

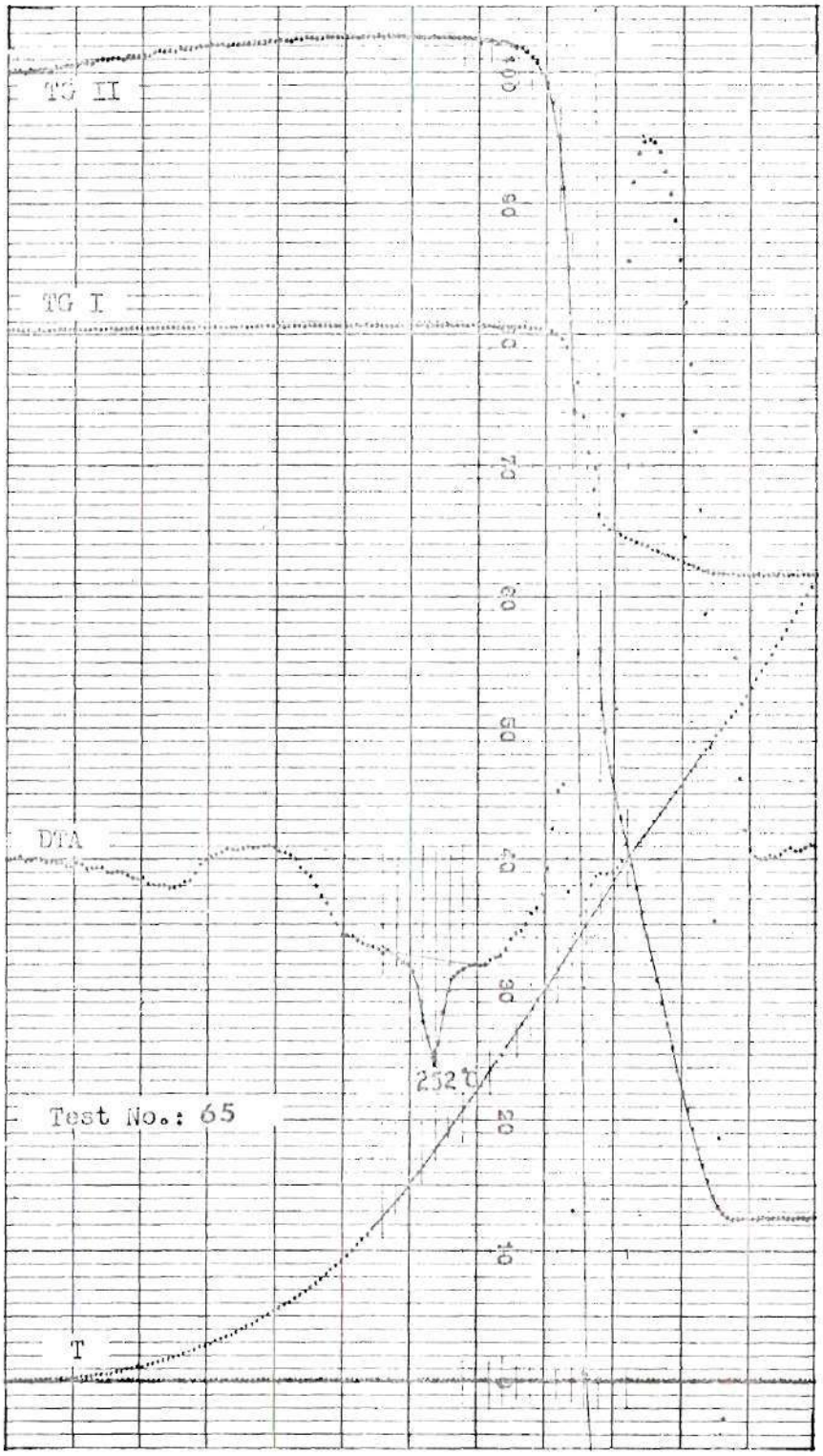


Figure 11. DTA/TGA Test of GIRCFF Fabric No. 2, Polyester, at $\emptyset$=25°C/min. (Linear Reduction=71%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/2/72 TEST NO.: 61

SAMPLE MATERIAL: GIRCFF NO. 5

SAMPLE AMOUNT: 20.1 MG.

DILUENT MATERIAL: GOLD POWDER

DILUENT AMOUNT: 79.7 MG.

REFERENCE MATERIAL: GOLD POWDER

REFERENCE AMOUNT: 99.7 MG.

THERMOCOUPLE: PT / PT-RH 10 %

HEATING RATE: 25 °C / MIN.

TEMPERATURE LIMITS: 25 TO 730 °C

GASEOUS ATMOSPHERE: AIR

FLOW RATE: 12 ML. / MIN.

CHART PAPER FEED RATE: 12 INCH / HR.

DTA SENSITIVITY: 5 μV / INCH

TG I SENSITIVITY: 10 MG. / INCH

TG II SENSITIVITY: 1 MG. / INCH

TEST INITIATION TIME: 11:55

REMARKS: _____

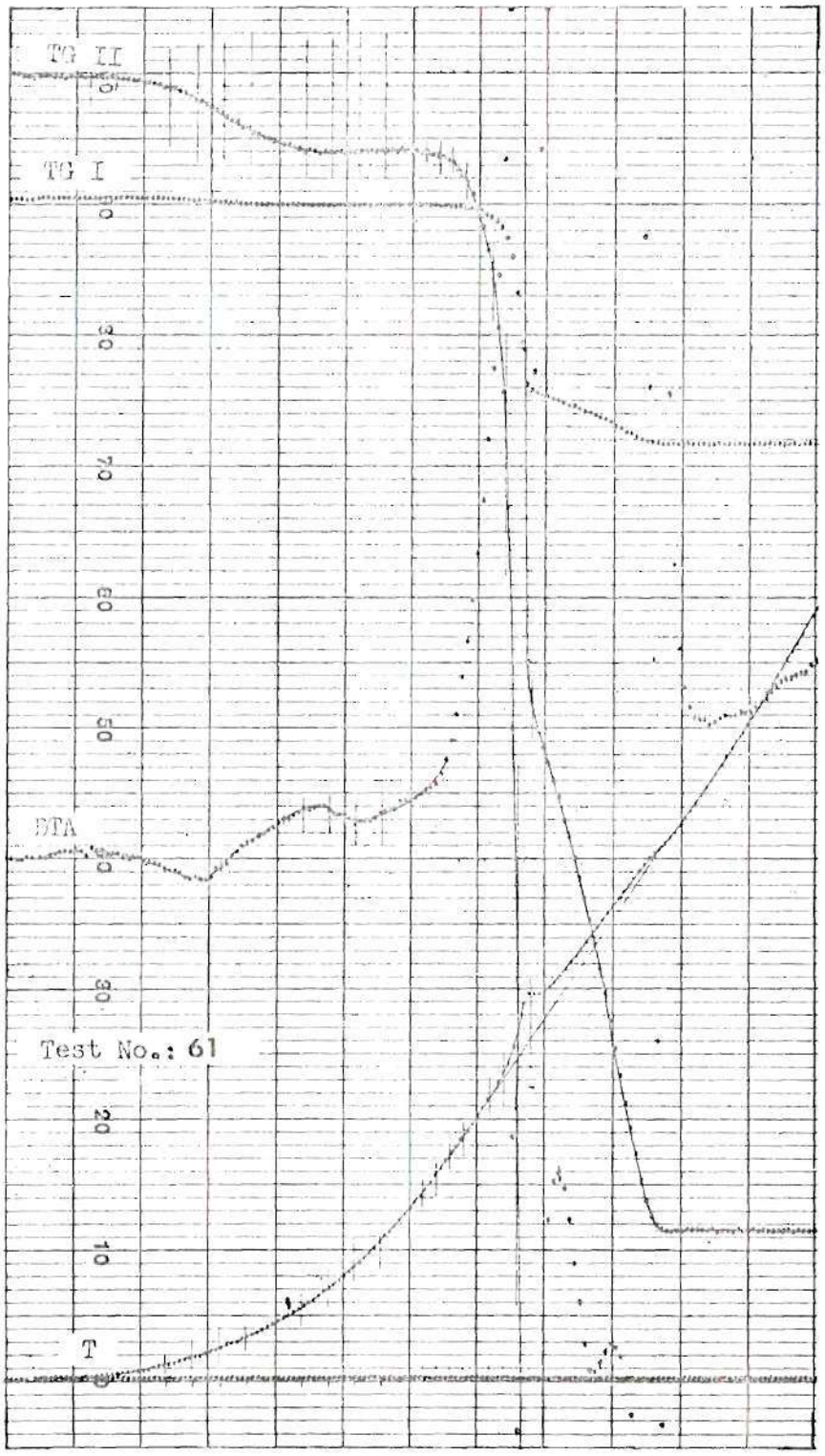


Figure 12. DTA/TGA Test of GIRCFF Fabric No. 5, Cotton, at $\emptyset$=25°C/min. (Linear Reduction=71%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/4/72 TEST NO.: 13

SAMPLE MATERIAL: GIRCFF NO. 5

SAMPLE AMOUNT: 20.0 Mg.

DILUENT MATERIAL: Gold Powder

DILUENT AMOUNT: 79.9 MG.

REFERENCE MATERIAL: Gold Powder

REFERENCE AMOUNT: 99.6 MG.

THERMOCOUPLE: Pt / Pt - Rh 10 %

HEATING RATE: 10 °C / Min.

TEMPERATURE LIMITS: 25 TO 510 °C

GASEOUS ATMOSPHERE: Air

FLOW RATE: 12 Ml. / Min.

CHART PAPER FEED RATE: 12 Inch / Hr.

DTA SENSITIVITY: 5 μV / Inch

TG I SENSITIVITY: 10 Mg. / Inch

TG II SENSITIVITY: 1 Mg. / Inch

TEST INITIATION TIME: 13:45

REMARKS: _____

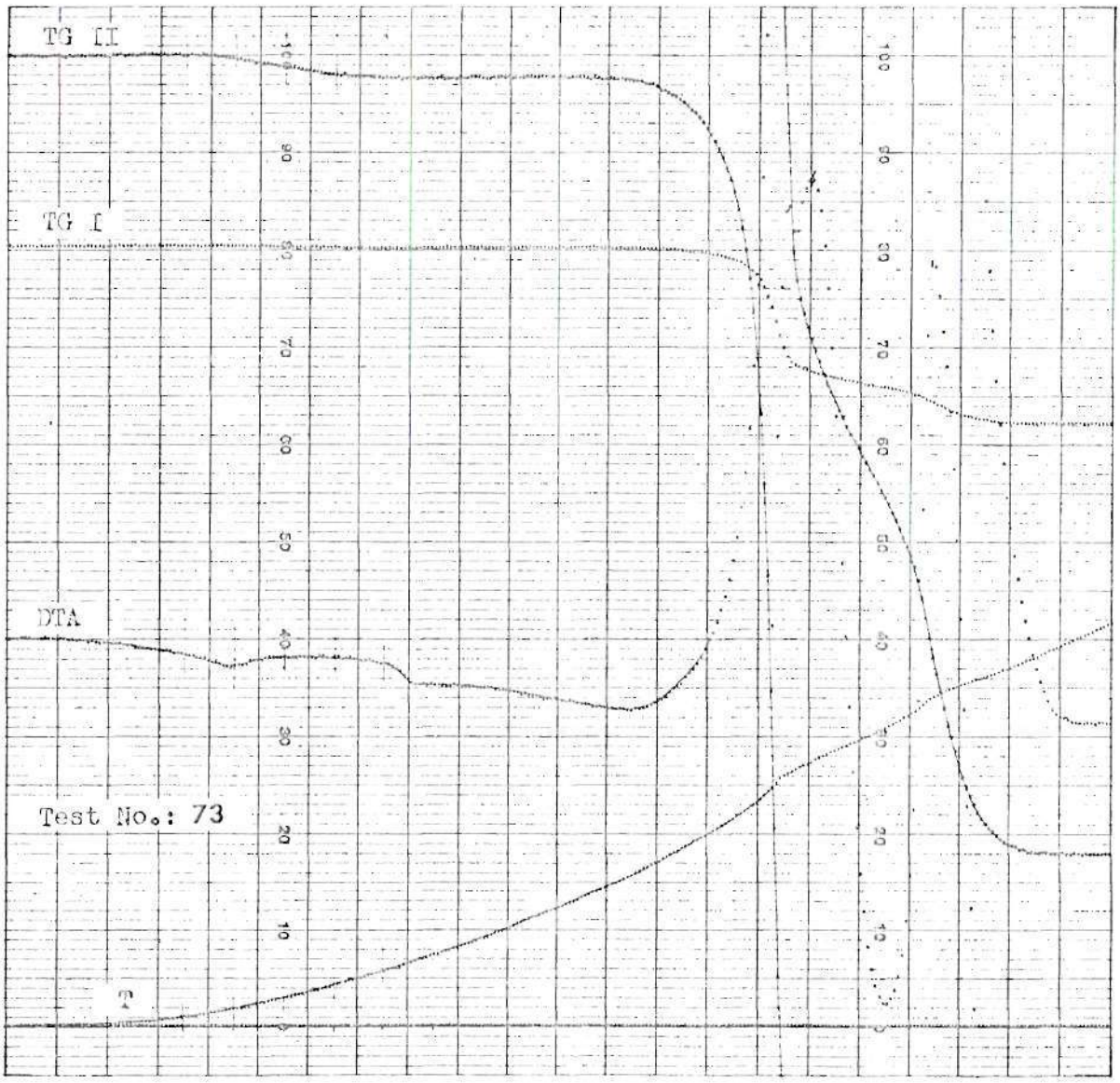


Figure 13. DTA/TGA Test of CIRCFF Fabric No. 5, Cotton at ϕ=10°C/min. (Linear Reduction=54%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/3/72 TEST NO.: 69

SAMPLE MATERIAL : GIRCEF NO. 8

SAMPLE AMOUNT : 20.1 Mg.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 79.9 MG.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.9 MG.

THERMOCOUPLE : PT / PT-RH 10 %

HEATING RATE : 25 °C / MIN.

TEMPERATURE LIMITS : 25 TO 1600 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 ML. / MIN.

CHART PAPER FEED RATE : 12 INCH / HR.

DTA SENSITIVITY : 5 μV / INCH

TG I SENSITIVITY : 10 MG. / INCH

TG II SENSITIVITY : 1 MG. / INCH

TEST INITIATION TIME : 15:35

REMARKS : _____

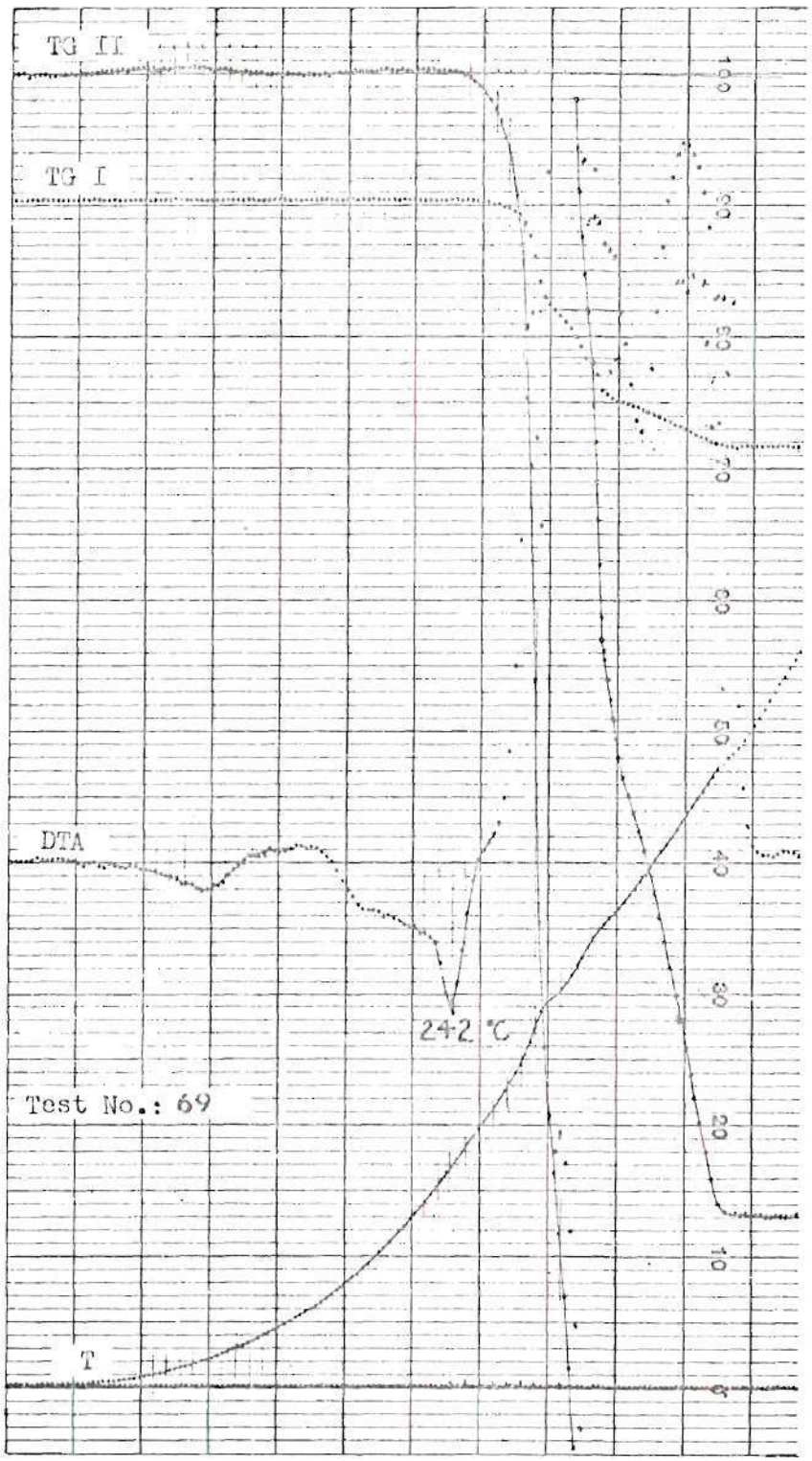


Figure 14. DTA/TGA Test of GIRCFF Fabric No. 8, Cotton-Polyester Blend, at $\emptyset$=25°C/min. (Linear Reduction=71%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/2/72 TEST NO.: 62

SAMPLE MATERIAL : GIRCEF NO. 10

SAMPLE AMOUNT : 19.7 MG.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 79.7 MG.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.8 MG.

THERMOCOUPLE : PT / PT - RH 10 %

HEATING RATE : 25 °C / MIN.

TEMPERATURE LIMITS : 25 TO 690 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 ML. / MIN.

CHART PAPER FEED RATE : 12 INCH / HR.

DTA SENSITIVITY : 5 μV / INCH

TG I SENSITIVITY : 10 MG. / INCH

TG II SENSITIVITY : 1 MG. / INCH

TEST INITIATION TIME : 14:15

REMARKS : _____

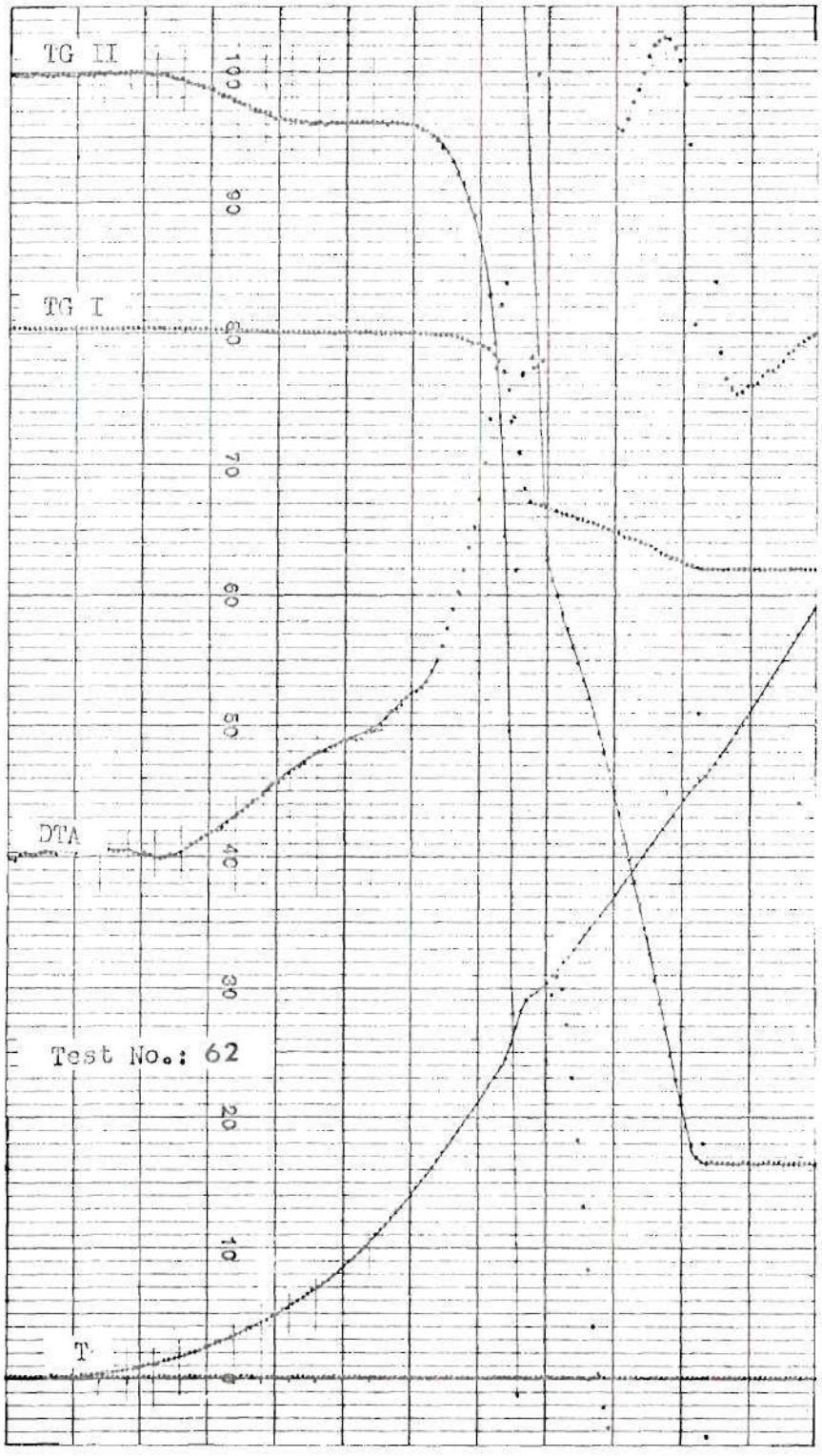


Figure 15. DTA/TGA Test of GIRCFF Fabric No. 10, Cotton, at ϕ=25°C/min. (Linear Reduction=71%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/7/12 TEST NO.: 74

SAMPLE MATERIAL : GIRGFF NO. 10

SAMPLE AMOUNT : 19.8 MG.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 79.7 MG.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.3 MG.

THERMOCOUPLE : PT / PT - RH 10 %

HEATING RATE : 10 °C / MIN.

TEMPERATURE LIMITS : 25 TO 530 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 ML. / MIN.

CHART PAPER FEED RATE : 12 INCH / HR.

DTA SENSITIVITY : 5 μV / INCH

TG I SENSITIVITY : 10 MG. / INCH

TG II SENSITIVITY : 1 MG. / INCH

TEST INITIATION TIME : 10:05

REMARKS : _____

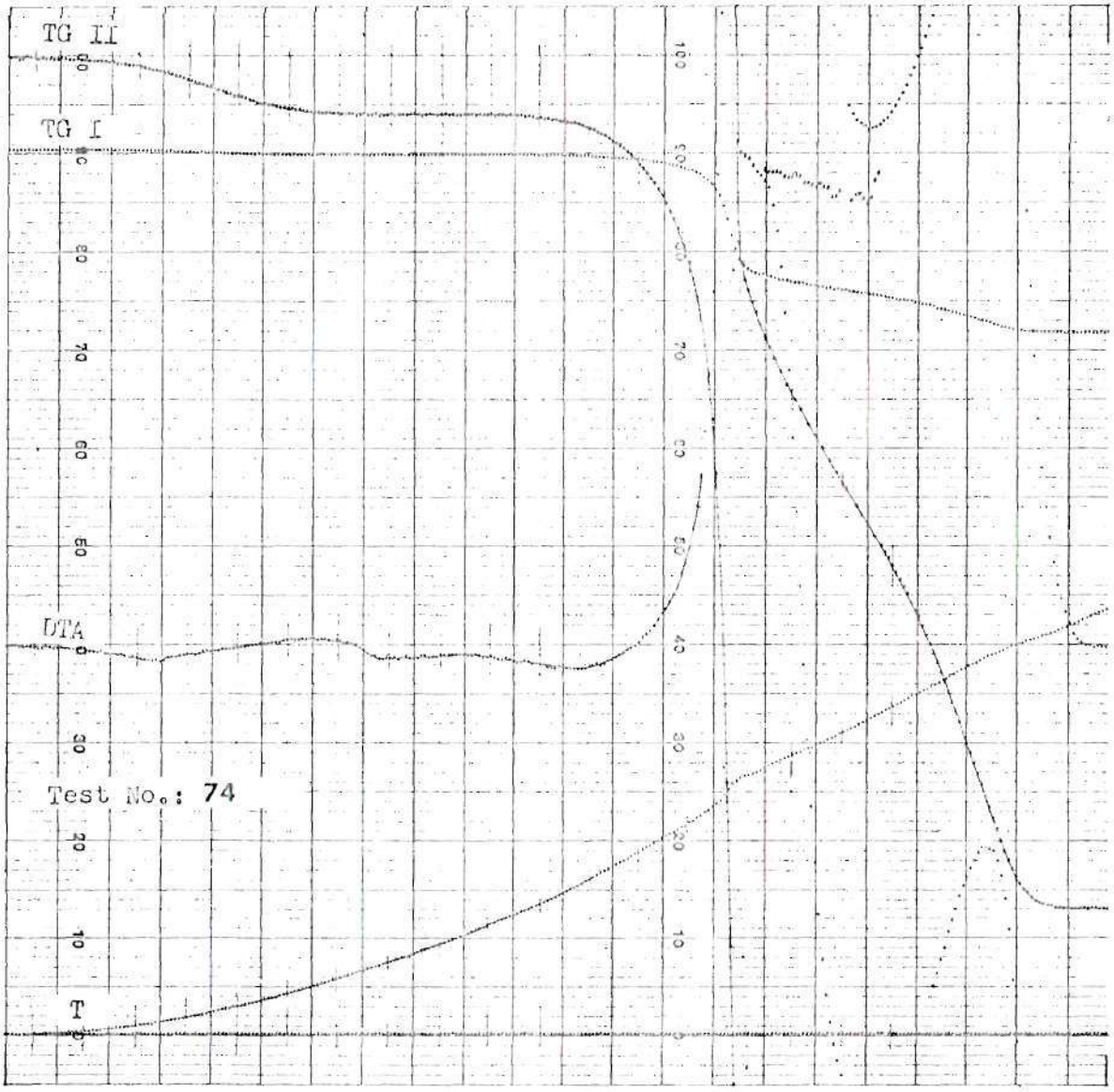


Figure 16. DTA/TGA Test of GIRCFF Fabric No. 10, Cotton, at $\emptyset$=10°C/min. (Linear Reduction=54%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/4/72 TEST NO.: 70

SAMPLE MATERIAL : CIRCEE NO. 11

SAMPLE AMOUNT : 20.5 MG.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 79.7 MG.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.4 MG.

THERMOCOUPLE : PT / PT - RH 10 %

HEATING RATE : 2.5 °C / MIN.

TEMPERATURE LIMITS : 25 TO 725 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 ML. / MIN.

CHART PAPER FEED RATE : 12 INCH / HR.

DTA SENSITIVITY : 5 μV / INCH

TG I SENSITIVITY : 10 MG. / INCH

TG II SENSITIVITY : 1 MG. / INCH

TEST INITIATION TIME : 8:25

REMARKS : _____

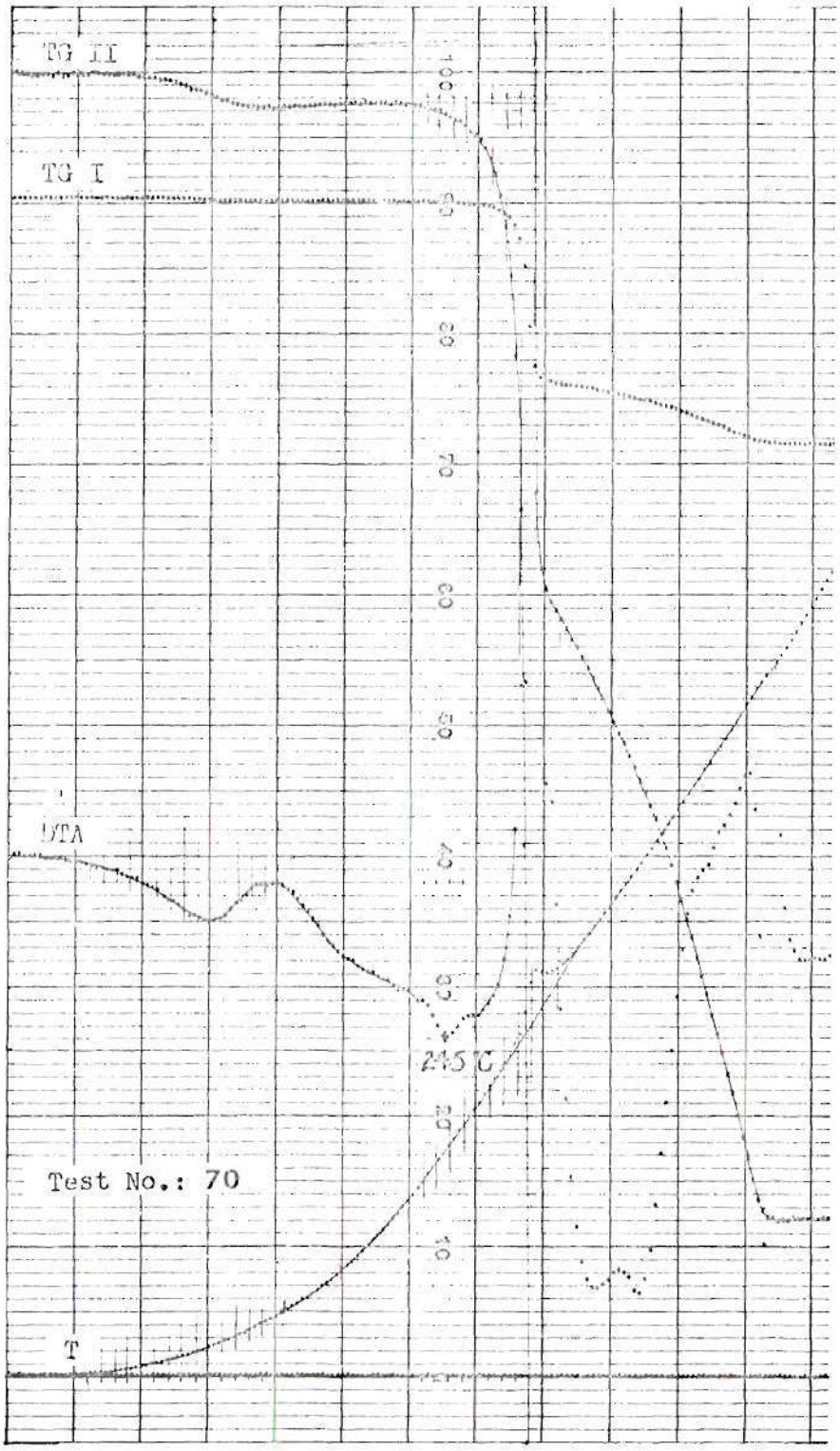


Figure 17. DTA/TGA Test of GIRCFF Fabric No. 11, Nylon--Acetate Blend, at $\emptyset$=25°C/min. (Linear Reduction=71%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/3/72 TEST NO.: 1a/b

SAMPLE MATERIAL : GIRGEE NO. 12

SAMPLE AMOUNT : 20.2 Mg.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 79.1a Mg.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.7 Mg.

THERMOCOUPLE : Pt / Pt-Rh 10 %

HEATING RATE : 25 °C / Min.

TEMPERATURE LIMITS : 25 TO 740 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 Ml. / Min.

CHART PAPER FEED RATE : 12 Inch / Hr.

DTA SENSITIVITY : 5 μV / Inch

TG I SENSITWITY : 10 Mg. / Inch

TG II SENSITIVITY : 1 Mg. / Inch

TEST INITIATION TIME : 11:45

REMARKS : _____

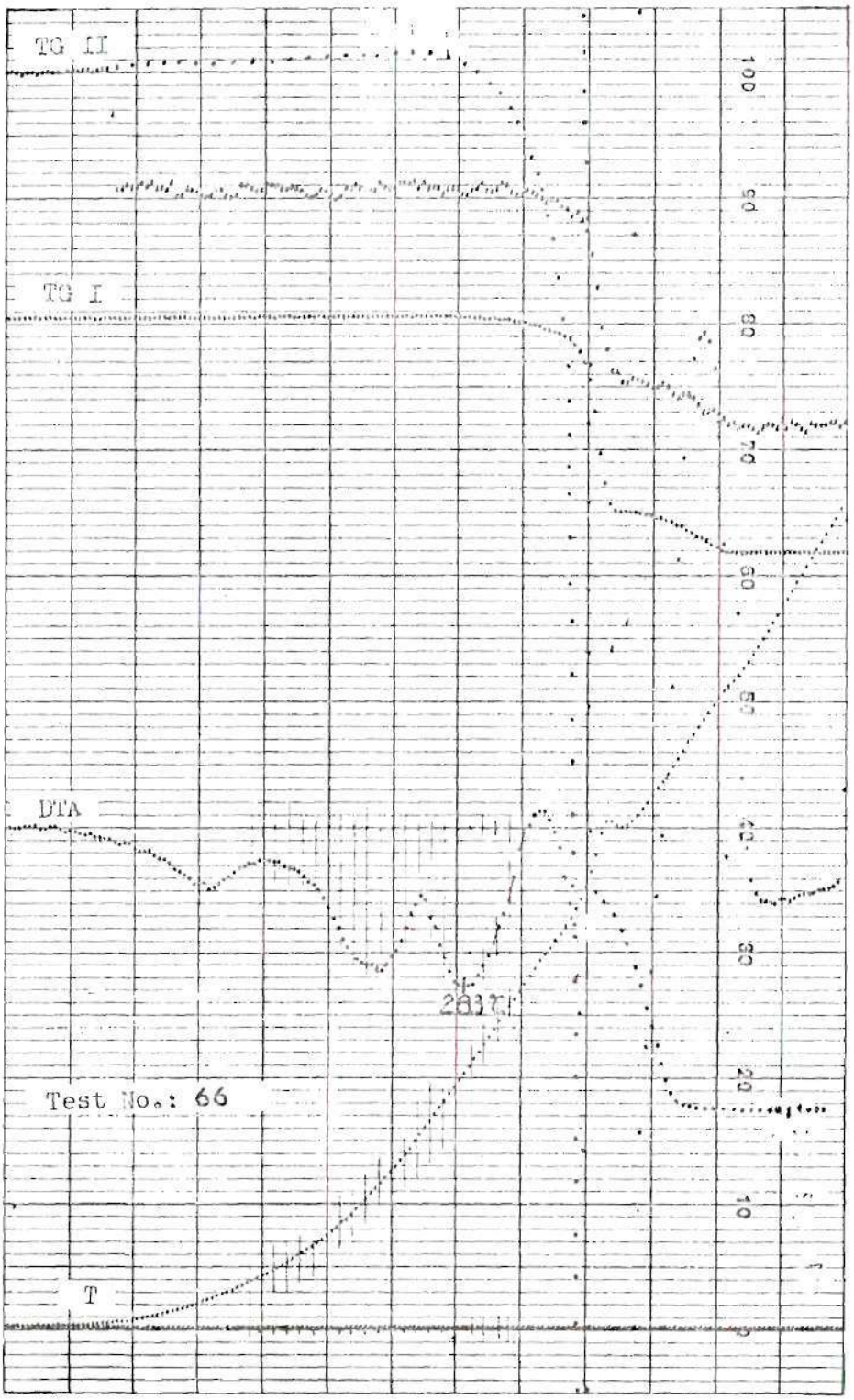


Figure 18. DTA/TGA Test of GIRCFF Fabric No. 12, Nylon, at Ø=25°C/min. (Linear Reduction=71%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/4/72 TEST NO.: 71

SAMPLE MATERIAL : GIRGFF NO. 17

SAMPLE AMOUNT : 20.0 MG.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 80.1 MG.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.8 MG.

THERMOCOUPLE : PT / PT - RH 10 %

HEATING RATE : 25 °C / MIN.

TEMPERATURE LIMITS : 25 TO 645 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 ML. / MIN.

CHART PAPER FEED RATE : 12 INCH / HR.

DTA SENSITIVITY : 5 μV / INCH

TG I SENSITIVITY : 10 MG. / INCH

TG II SENSITIVITY : 1 MG. / INCH

TEST INITIATION TIME : 10:10

REMARKS : _____

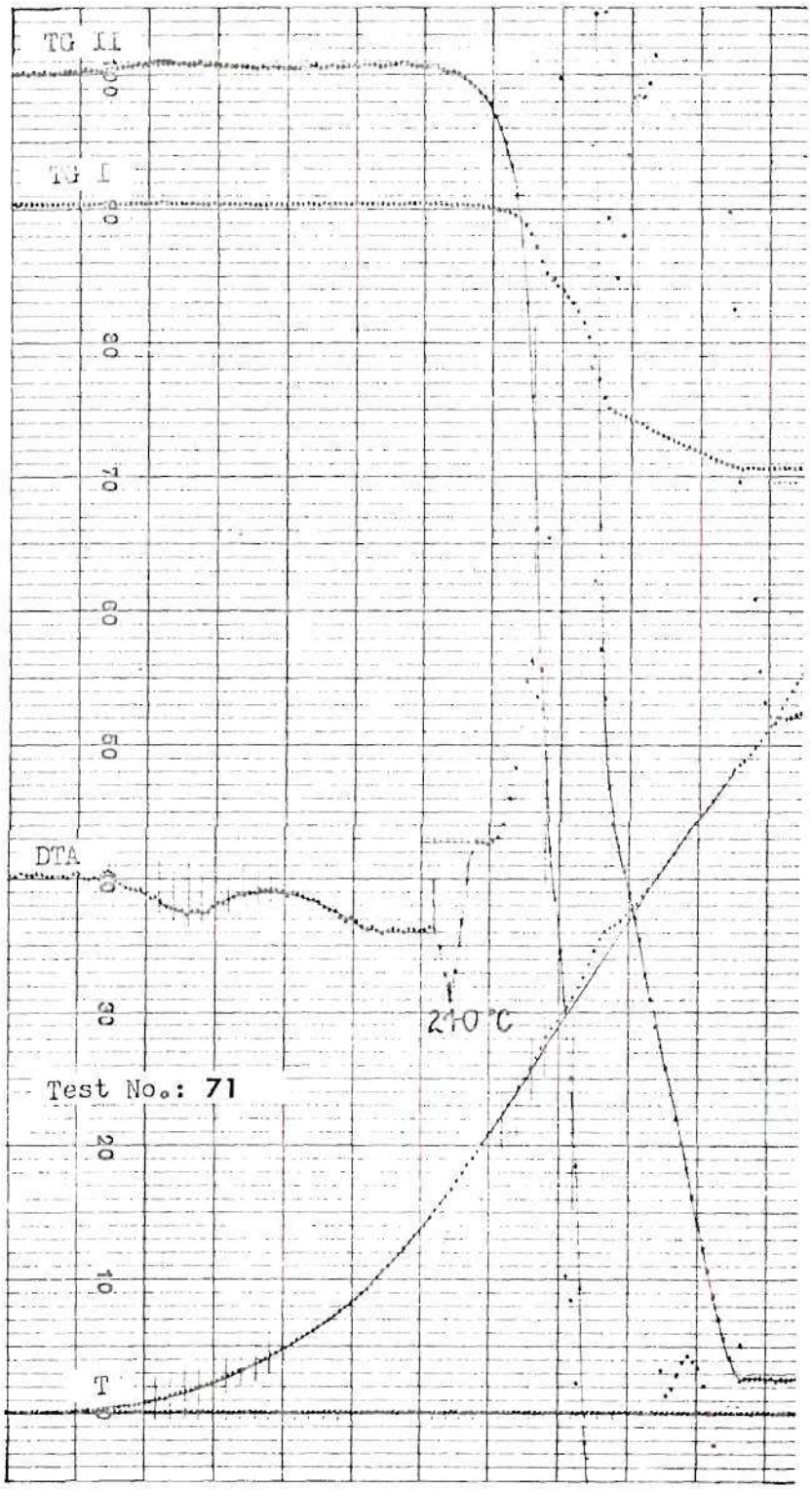


Figure 19. DTA/TGA Test of GIRCFF Fabric No. 17, Cotton-Polyester Blend, at Ø=25°C/min. (Linear Reduction=71%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/2/72 TEST NO.: 63

SAMPLE MATERIAL : CIRCEF NO. 18

SAMPLE AMOUNT : 20.2 MG.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 79.9 MG.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.5 MG.

THERMOCOUPLE : PT / PT-RH 10 %

HEATING RATE : 25 °C / MIN.

TEMPERATURE LIMITS : 25 TO 630 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 ML. / MIN.

CHART PAPER FEED RATE : 12 INCH / HR.

DTA SENSITIVITY : 5 μV / INCH

TG I SENSITIVITY : 10 MG. / INCH

TG II SENSITIVITY : 1 MG. / INCH

TEST INITIATION TIME : 15:50

REMARKS : _____

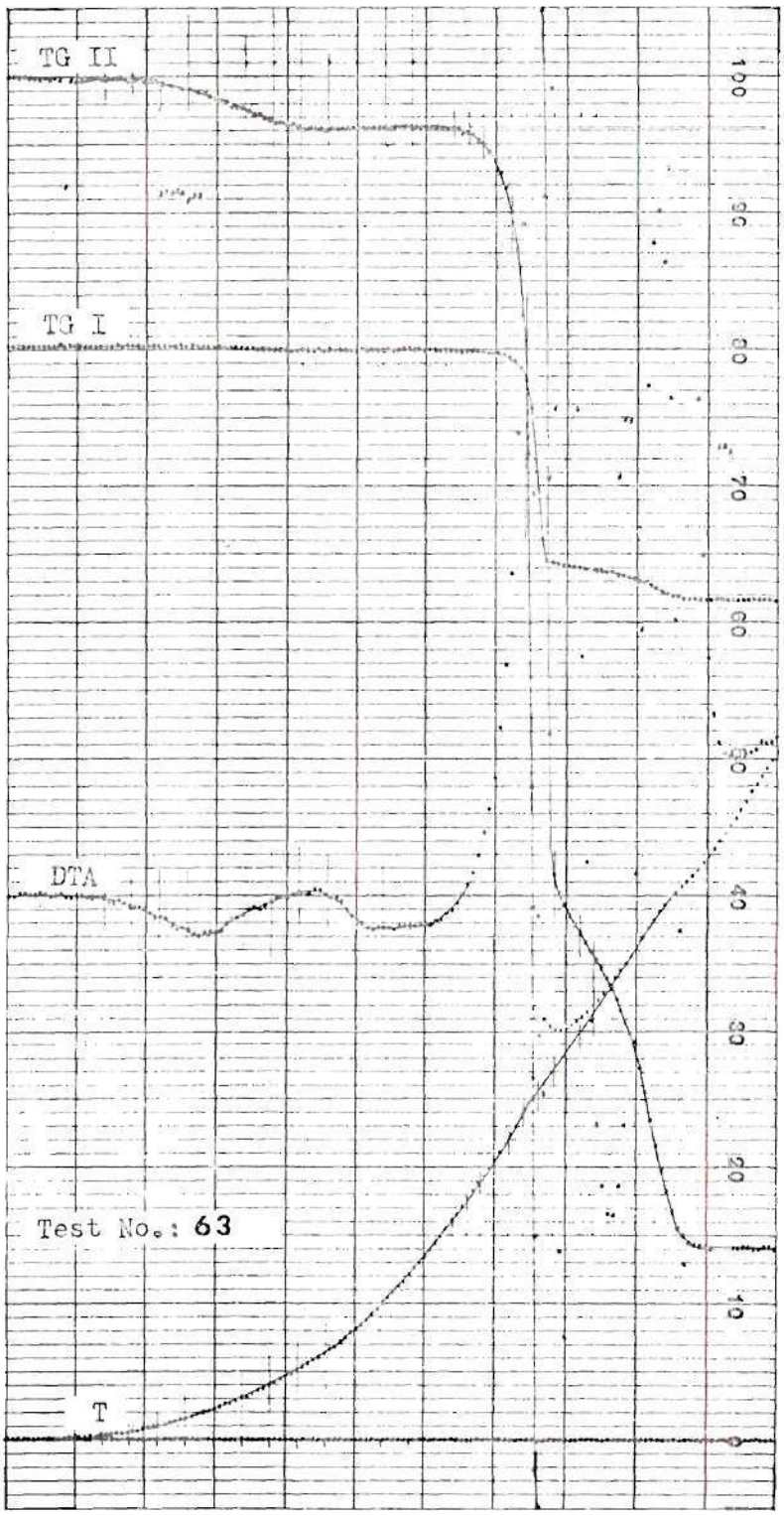


Figure 20. DTA/TGA Test of GIRCFF Fabric No. 18, Cotton, at $\emptyset$=25°C/min. (Linear Reduction=71%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/1/72 TEST NO.: 75

SAMPLE MATERIAL : GIRGEF NO. 18

SAMPLE AMOUNT : 20.2 MG.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 79.8 MG.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.6 MG.

THERMOCOUPLE : PT / PT - RH 10 %

HEATING RATE : 10 °C / MIN.

TEMPERATURE LIMITS : 25 TO 520 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 ML. / MIN.

CHART PAPER FEED RATE : 12 INCH / HR.

DTA SENSITIVITY : 5 μV / INCH

TG I SENSITIVITY : 10 MG. / INCH

TG II SENSITIVITY : 1 MG. / INCH

TEST INITIATION TIME : 11:50

REMARKS : _____

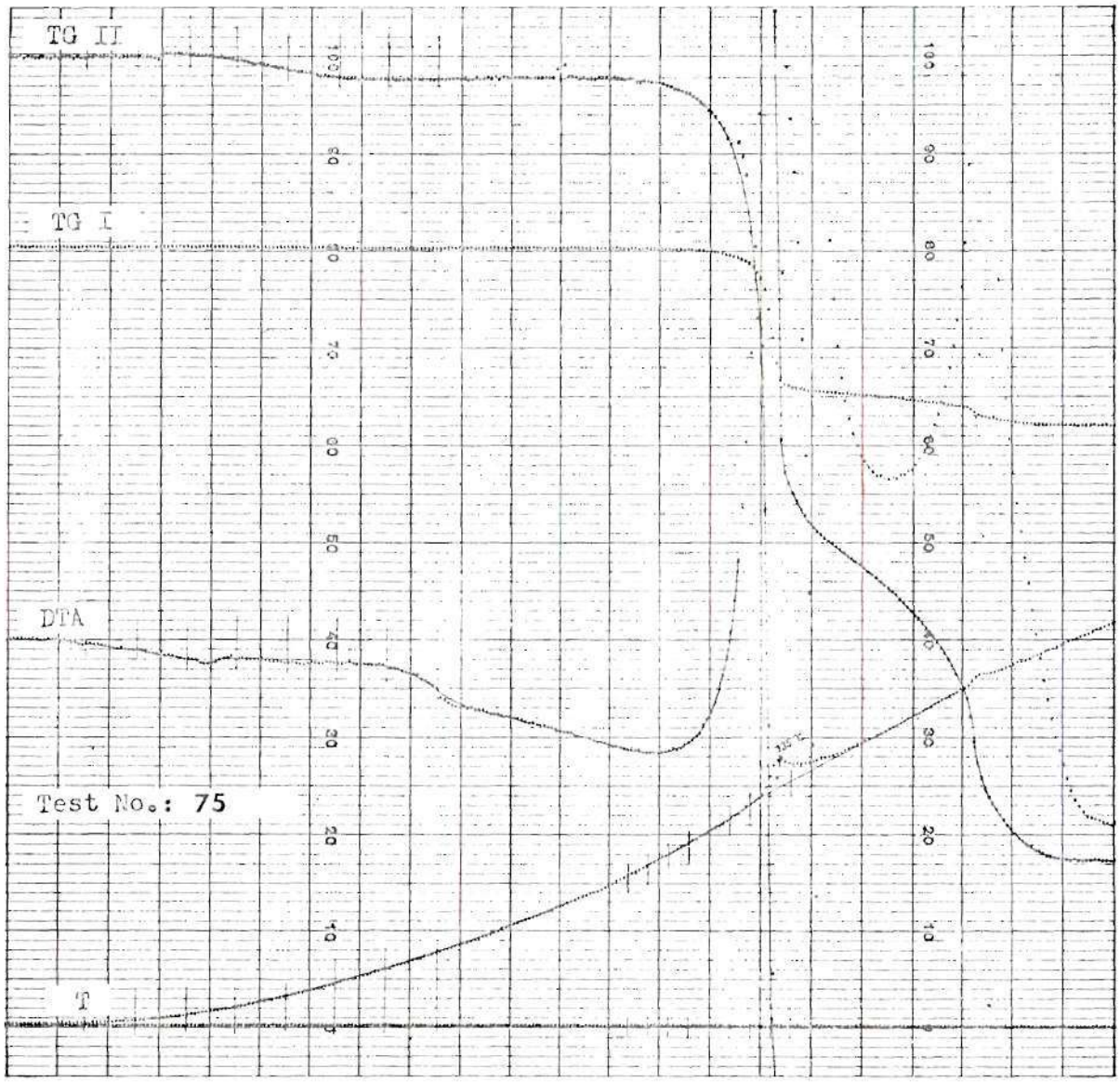


Figure 21. DTA/TGA Test of GIRCFF Fabric No. 18, Cotton at ϕ=10°C/min. (Linear Reduction=54%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/3/72 TEST NO.: 64

SAMPLE MATERIAL : GIRCEF NO. 19

SAMPLE AMOUNT : 19.8 Mg.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 79.1 Mg.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.9 Mg.

THERMOCOUPLE : Pt / Pt - Rh 10 %

HEATING RATE : 25 °C / Min.

TEMPERATURE LIMITS : 25 TO 840 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 Ml. / Min.

CHART PAPER FEED RATE : 12 Inch / Hr.

DTA SENSITIVITY : 5 μV / Inch

TG I SENSITIVITY : 10 Mg. / Inch

TG II SENSITIVITY : 1 Mg. / Inch

TEST INITIATION TIME : 8:30

REMARKS : _____

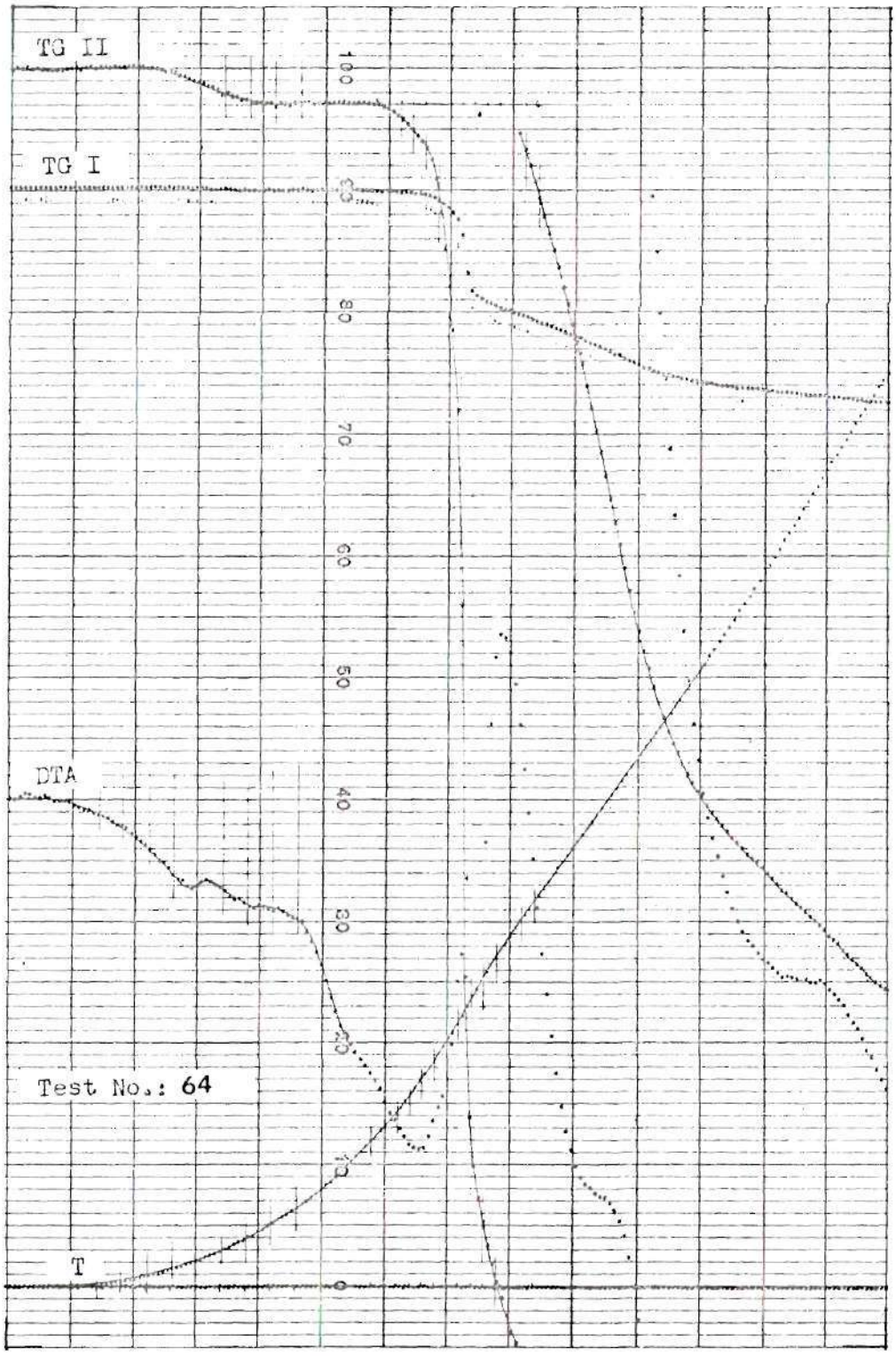


Figure 22. DTA/TGA Test of GIRCFF Fabric No. 19, Treated Cotton, at Ø=25°C/min. (Linear Reduction=71%)

GEORGIA INSTITUTE OF TECHNOLOGY - MECHANICAL ENGINEERING

FABRIC FLAMMABILITY PROJECT

DTA/TGA DATA SHEET

DATE: 8/7/72 TEST NO.: 76

SAMPLE MATERIAL : SIRCEF NO. 19

SAMPLE AMOUNT : 20.2 Mg.

DILUENT MATERIAL : GOLD POWDER

DILUENT AMOUNT : 80.0 Mg.

REFERENCE MATERIAL : GOLD POWDER

REFERENCE AMOUNT : 99.4 Mg.

THERMOCOUPLE : Pt / Pt - Rh 10 %

HEATING RATE : 10 °C / Min.

TEMPERATURE LIMITS : 25 TO 835 °C

GASEOUS ATMOSPHERE : AIR

FLOW RATE : 12 Ml. / Min.

CHART PAPER FEED RATE : 12 Inch / Hr.

DTA SENSITIVITY : 5 μV / Inch

TG I SENSITIVITY : 10 Mg. / Inch

TG II SENSITIVITY : 1 Mg. / Inch

TEST INITIATION TIME : 13:45

REMARKS : _____

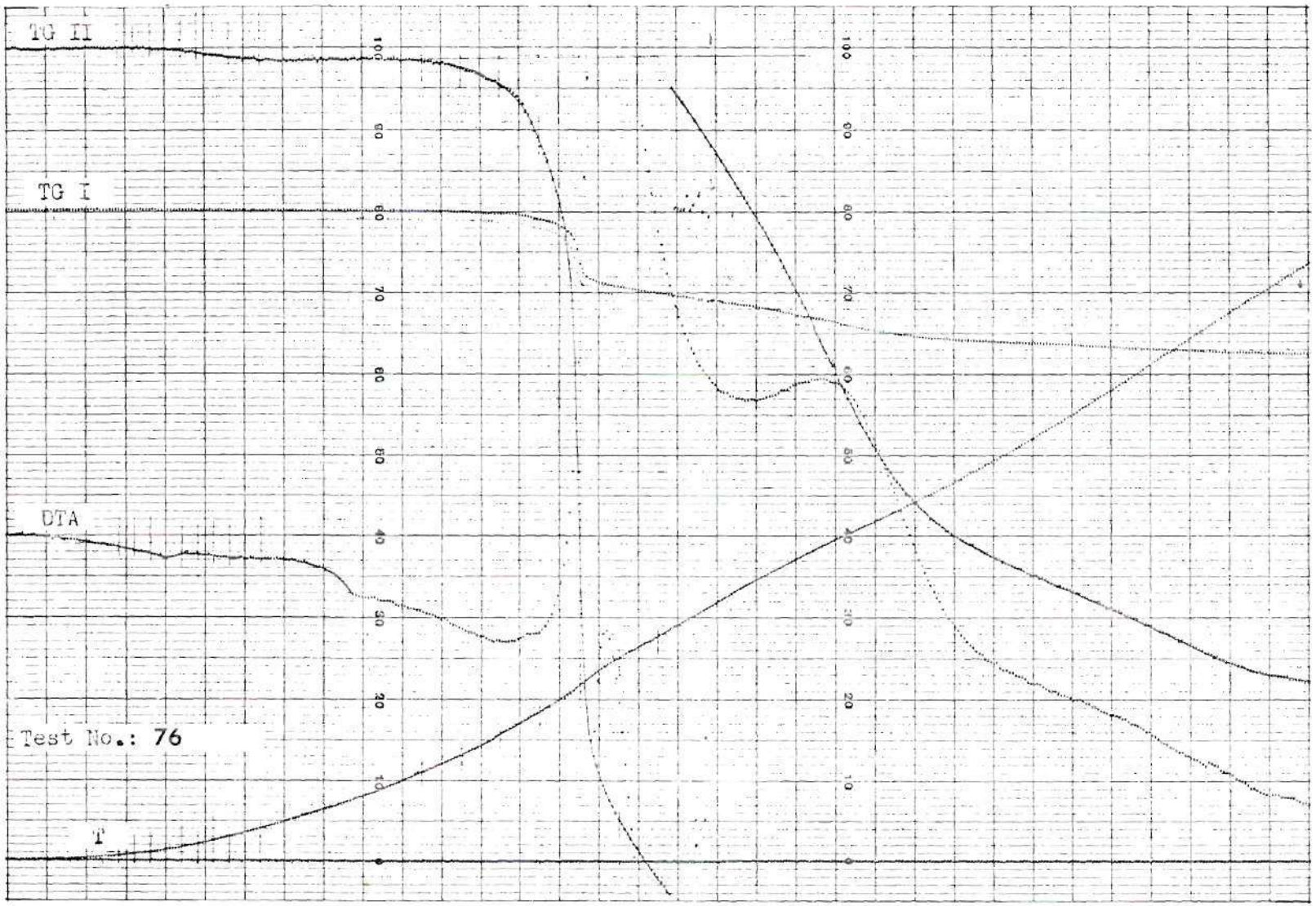


Figure 23. DTA/TGA Test of GIRCFF Fabric No. 19, Treated Cotton, at Ø=10°C/min. (Linear Reduction=50%)

APPENDIX C

LEAST-SQUARE LINES

This appendix contains the least-square lines used to evaluate the kinetic parameters for the endothermal moisture desorption of the GIRCFF fabrics and the decomposition reaction of the GIRCFF fabrics from McCarter's data. The least-square lines from Methods I and III are presented for the moisture desorption, while the least-square lines from Method I are presented for McCarter's data.

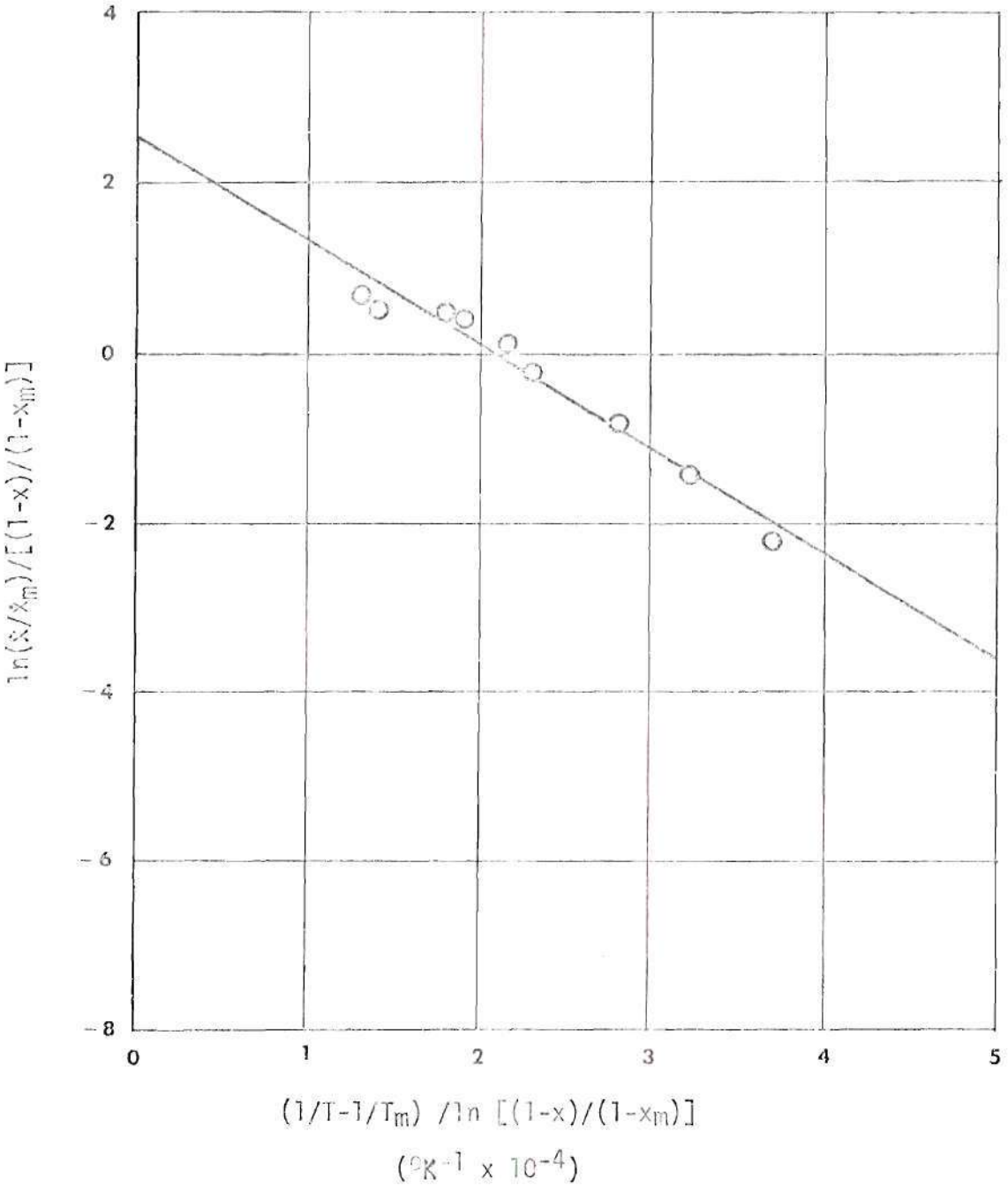


Figure 24. Least - Square Line for GIRCFF Fabric No. 5, Cotton, Evaluated by Method I for ϕ = 25°C/min.

(Temp. Range: 28-146°C)

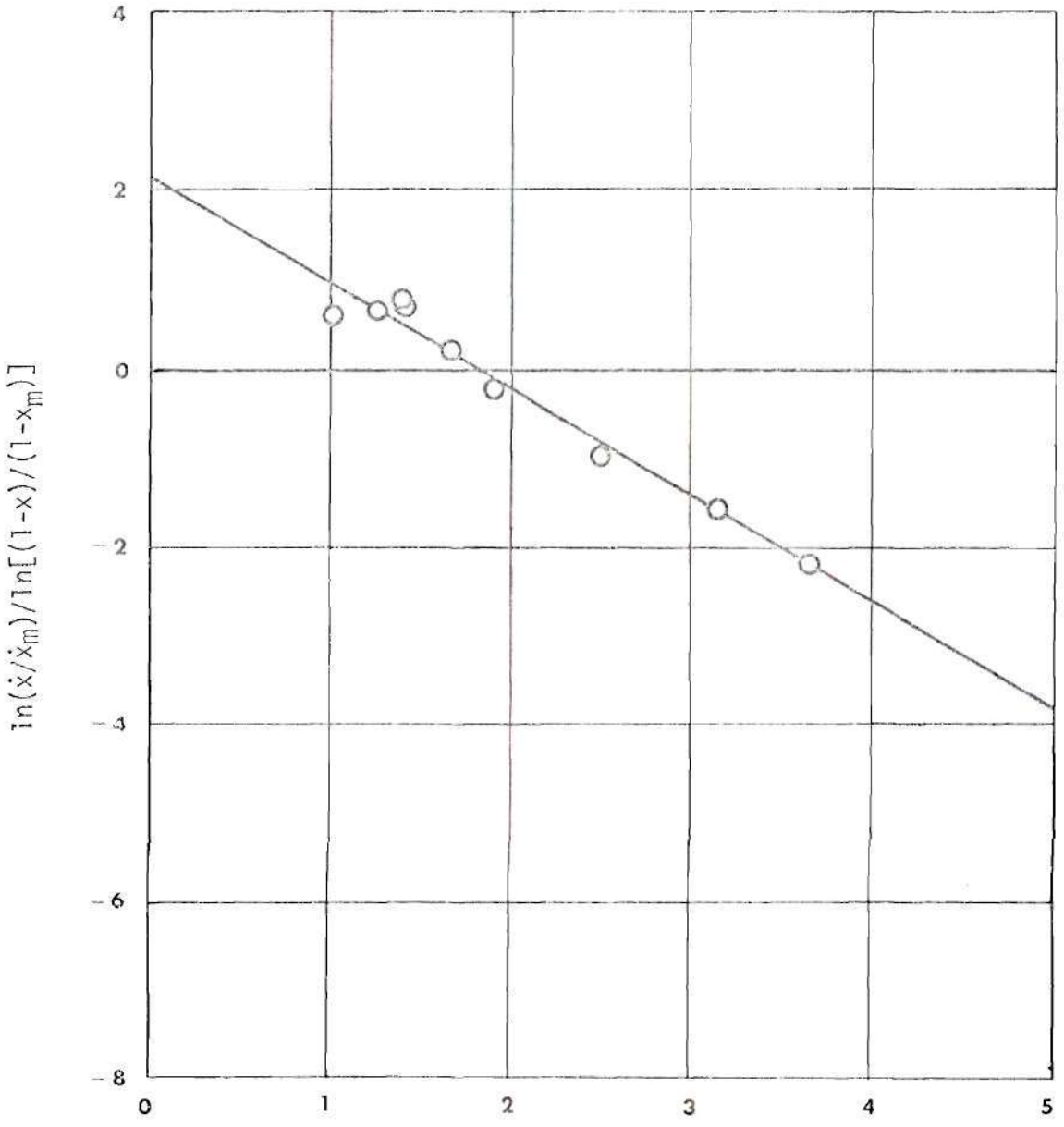


Figure 25. Least - Square Line for GIRCFF Fabric No. 5, Cotton, Evaluated by Method I for ϕ = 10°C/min.

(Temp. Range: 36-120°C)

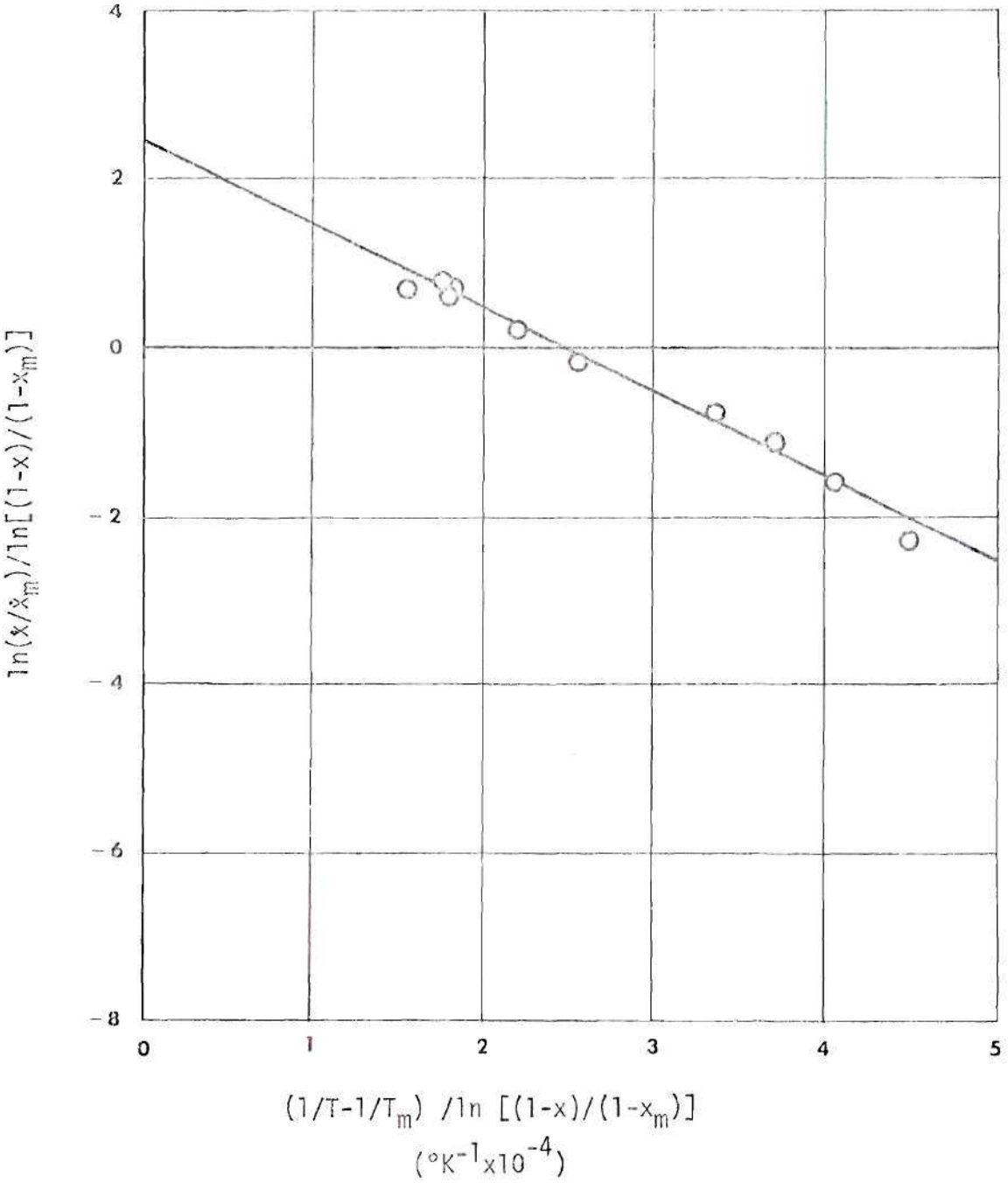


Figure 26. Least - Square Line for GIRCFF Fabric No. 10, Cotton, Evaluated by Method I for ϕ = 25°C/min.

(Temp. Range: 28-169°C)

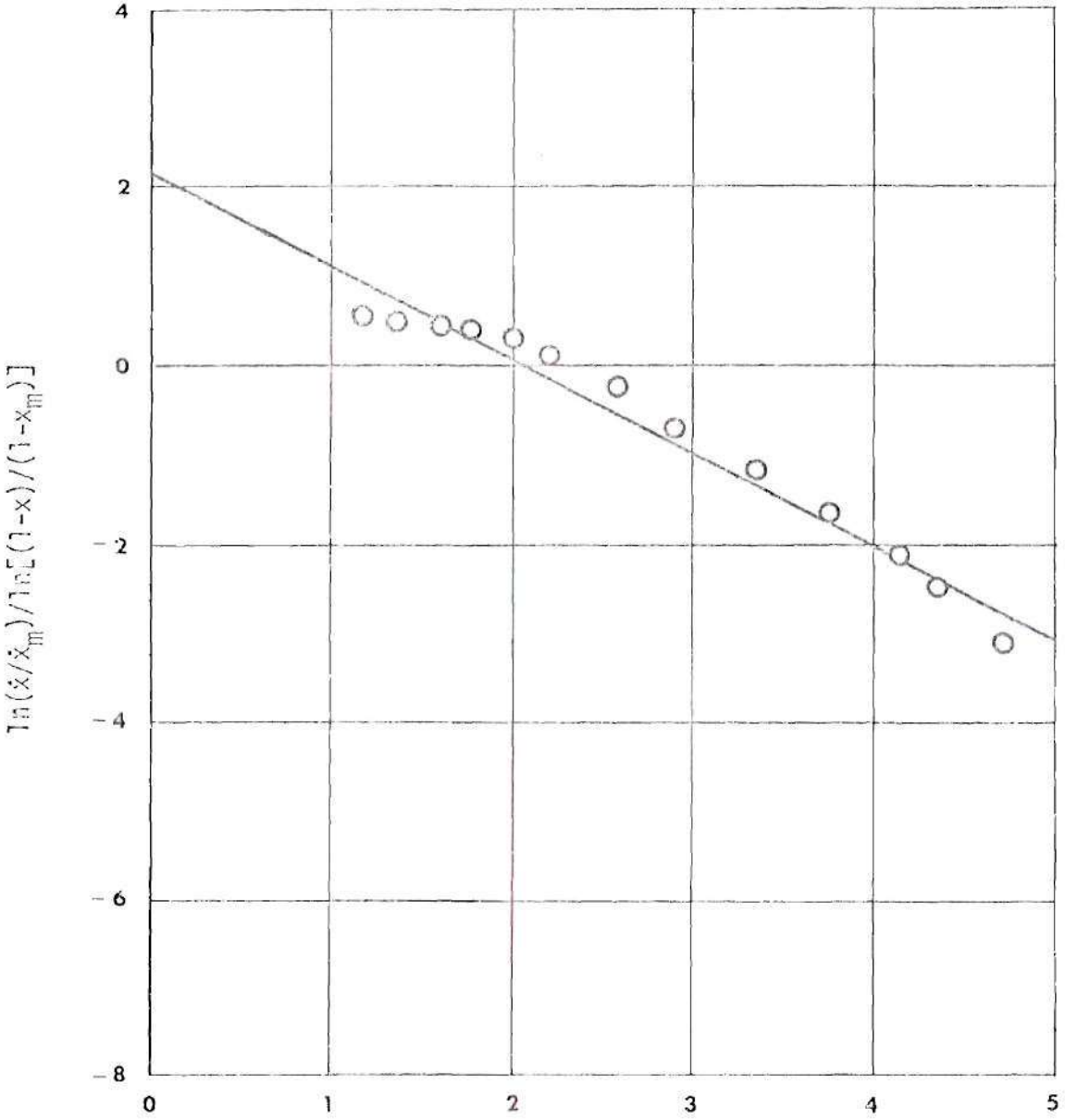


Figure 27. Least - Square Line for GIRCFF Fabric No. 10, Cotton, Evaluated by Method I for ϕ = 10°C/min.

(Temp. Range: 25-120°C)

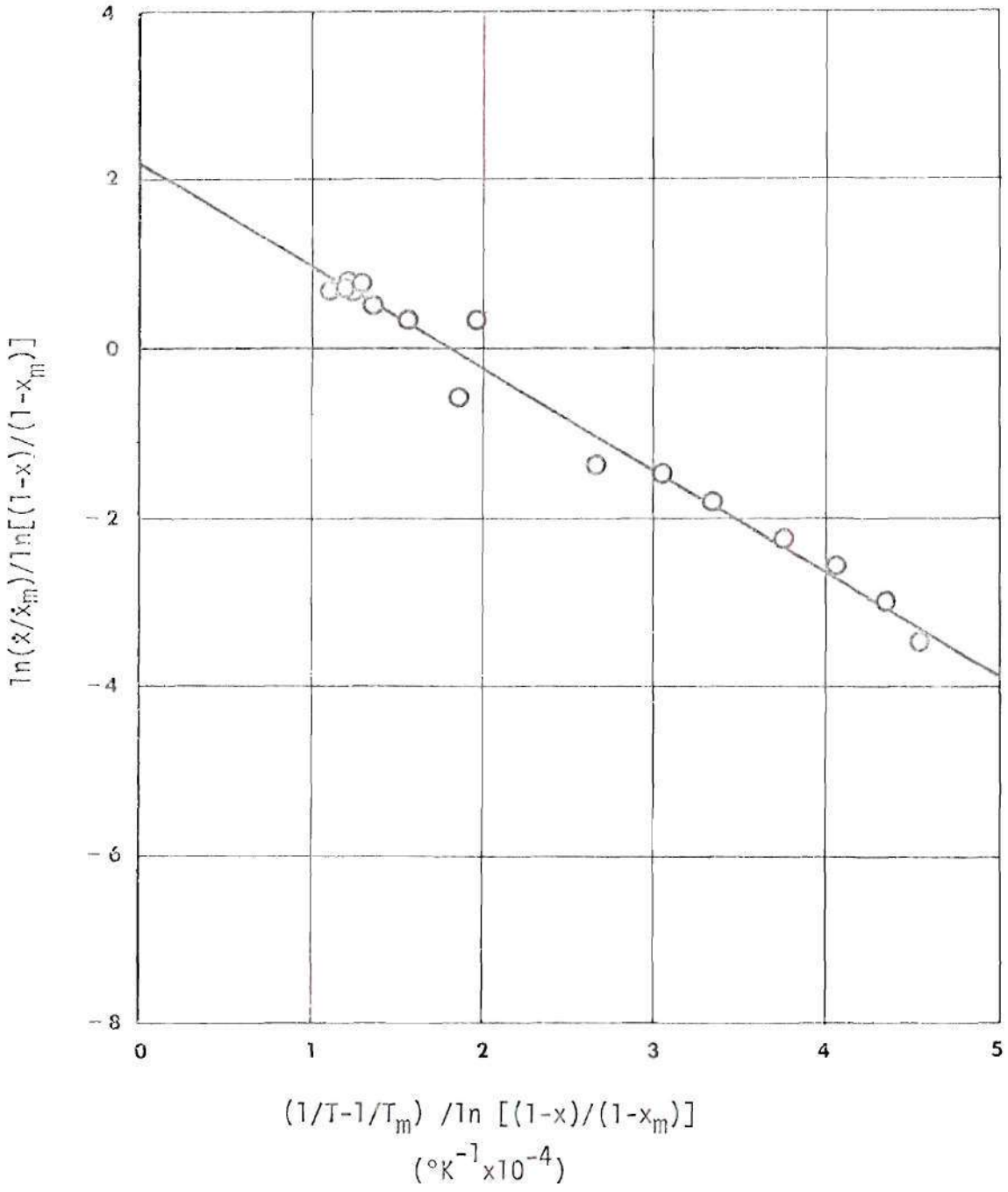


Figure 28. Least - Square Line for GIRCFF Fabric No. 18, Cotton, Evaluated by Method I for ϕ = 25°C/min.

(Temp. Range: 31-140°C)

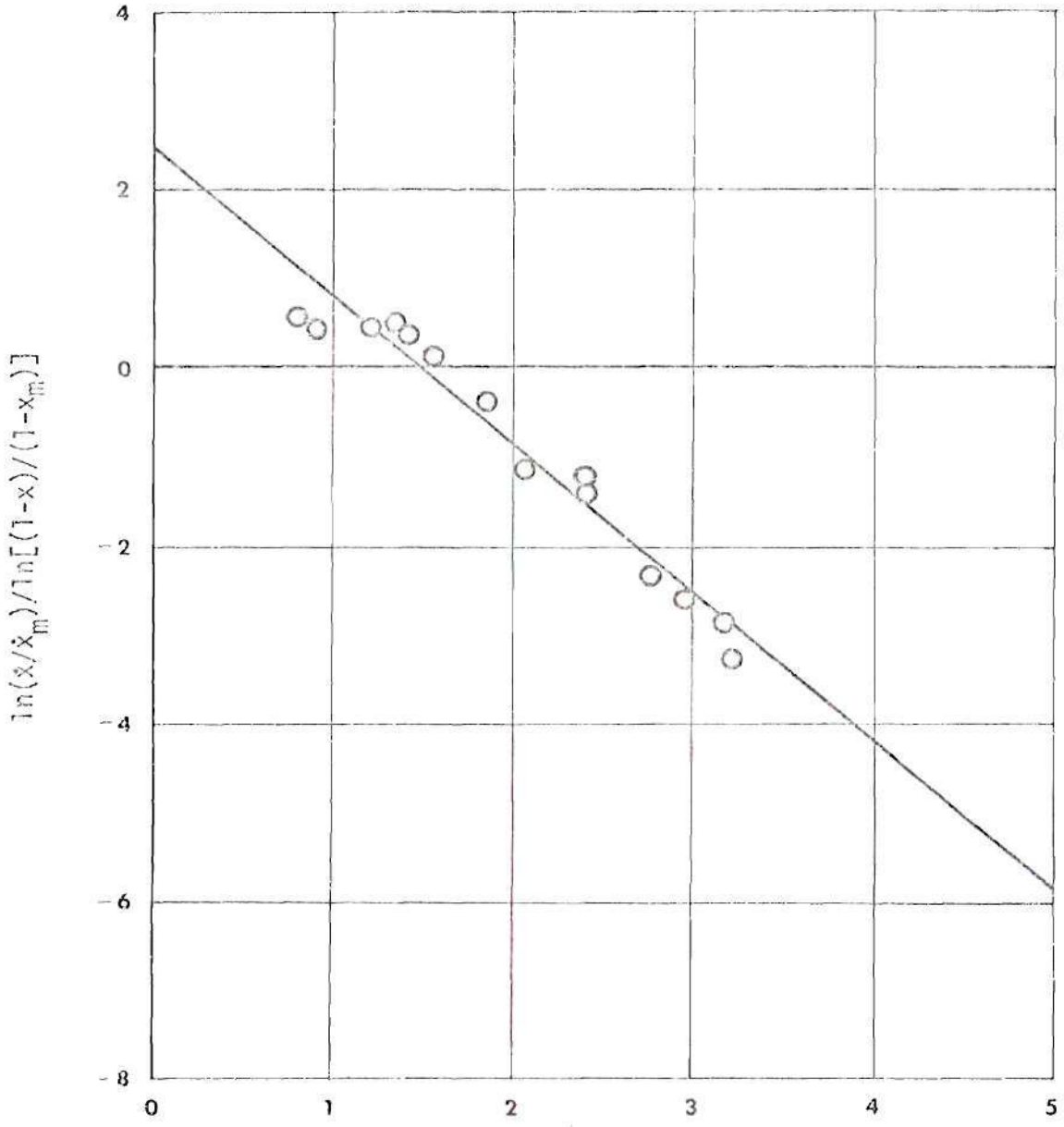


Figure 29. Least - Square Line for GIRCFF Fabric No. 18, Cotton, Evaluated by Method I for ϕ = 10°C/min.

(Temp. Range: 30-103°C)

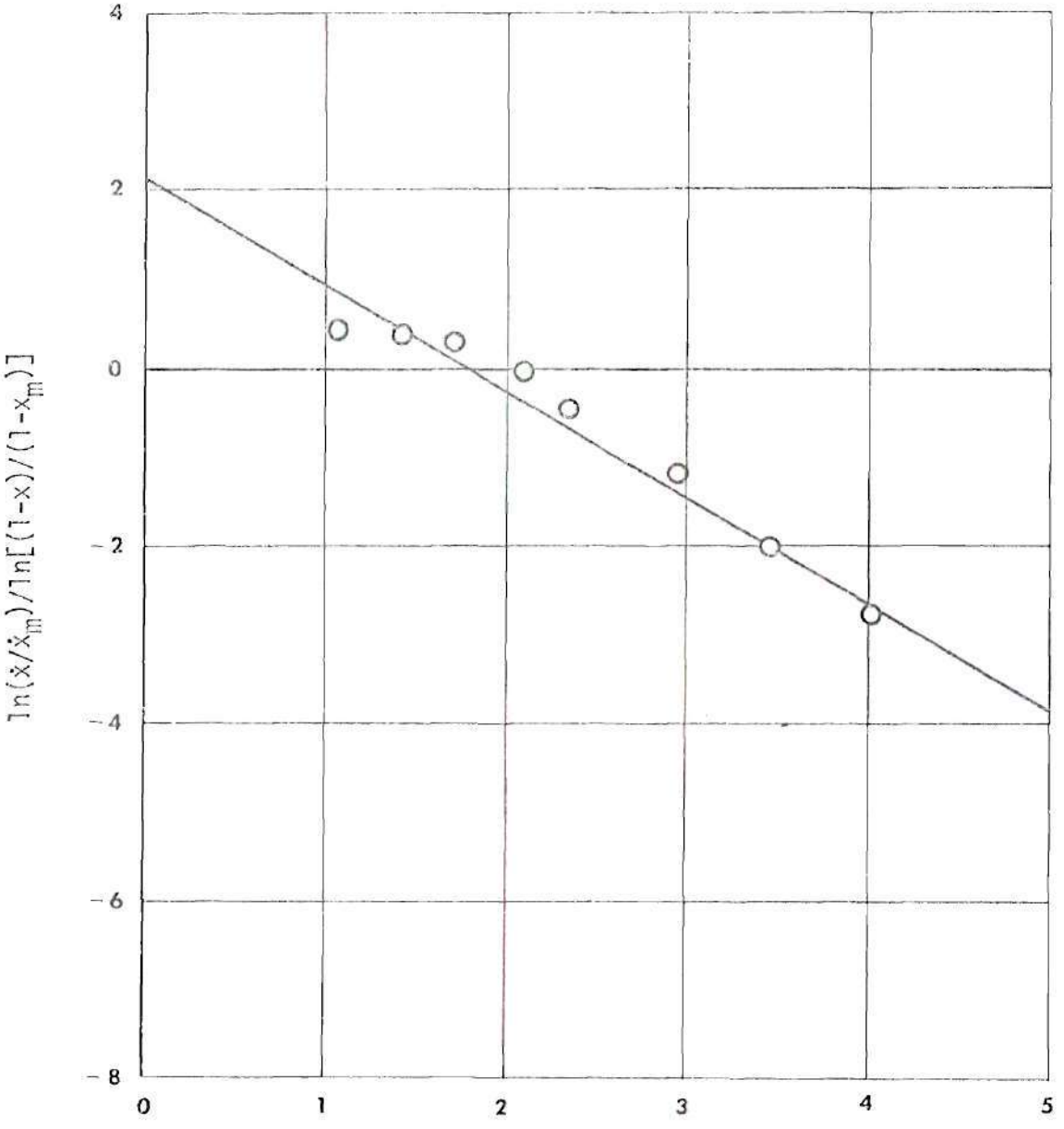


Figure 30. Least - Square Line for GIRCFF Fabric No. 19, Treated Cotton, Evaluated by Method I for ϕ = 25°C/min.

(Temp. Range: 28-120°C)

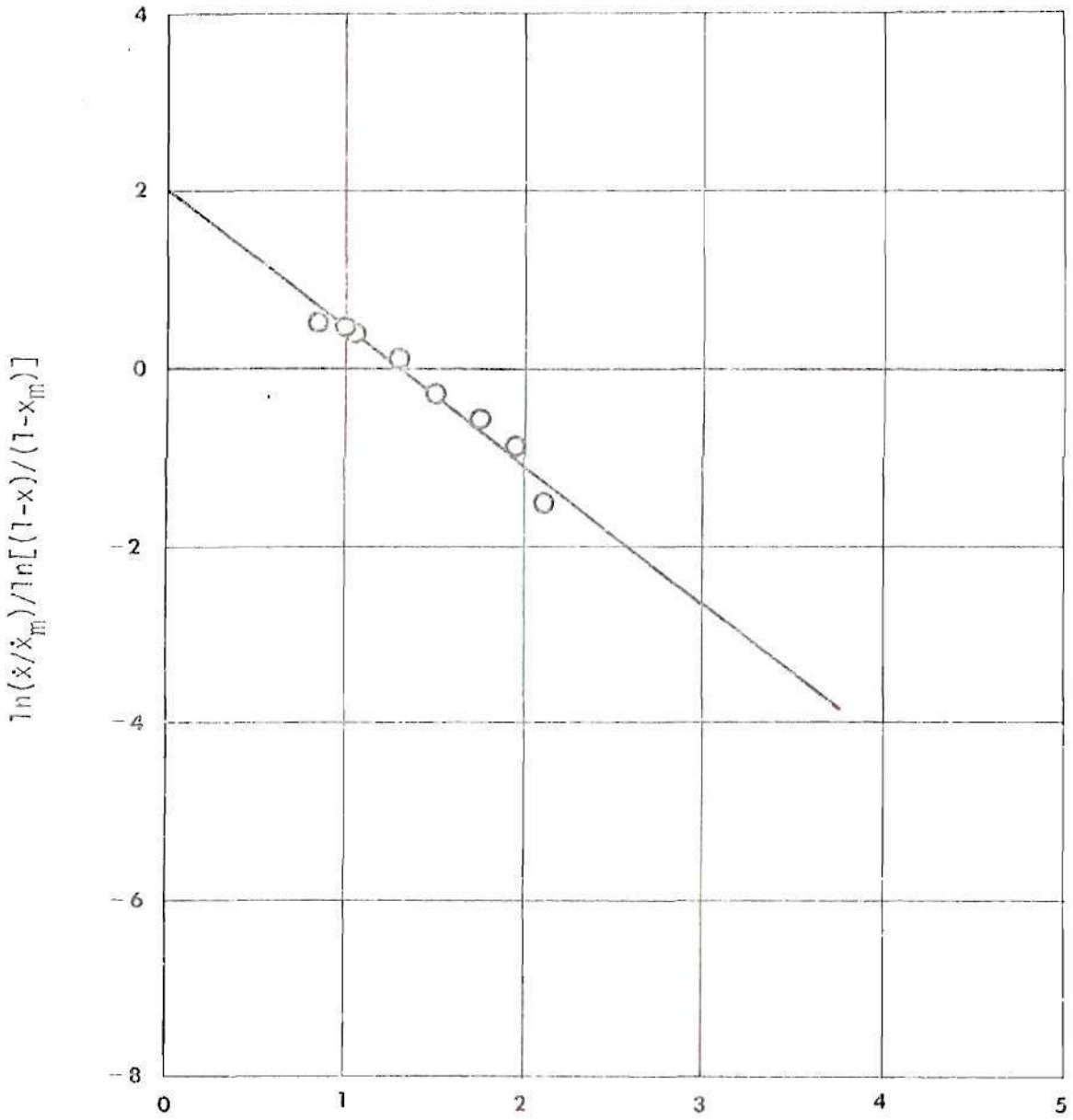


Figure 31. Least - Square Line for GIRCFF Fabric No. 19, Treated Cotton, Evaluated by Method I for ϕ = 10°C/min.

(Temp. Range: 35-90°C)

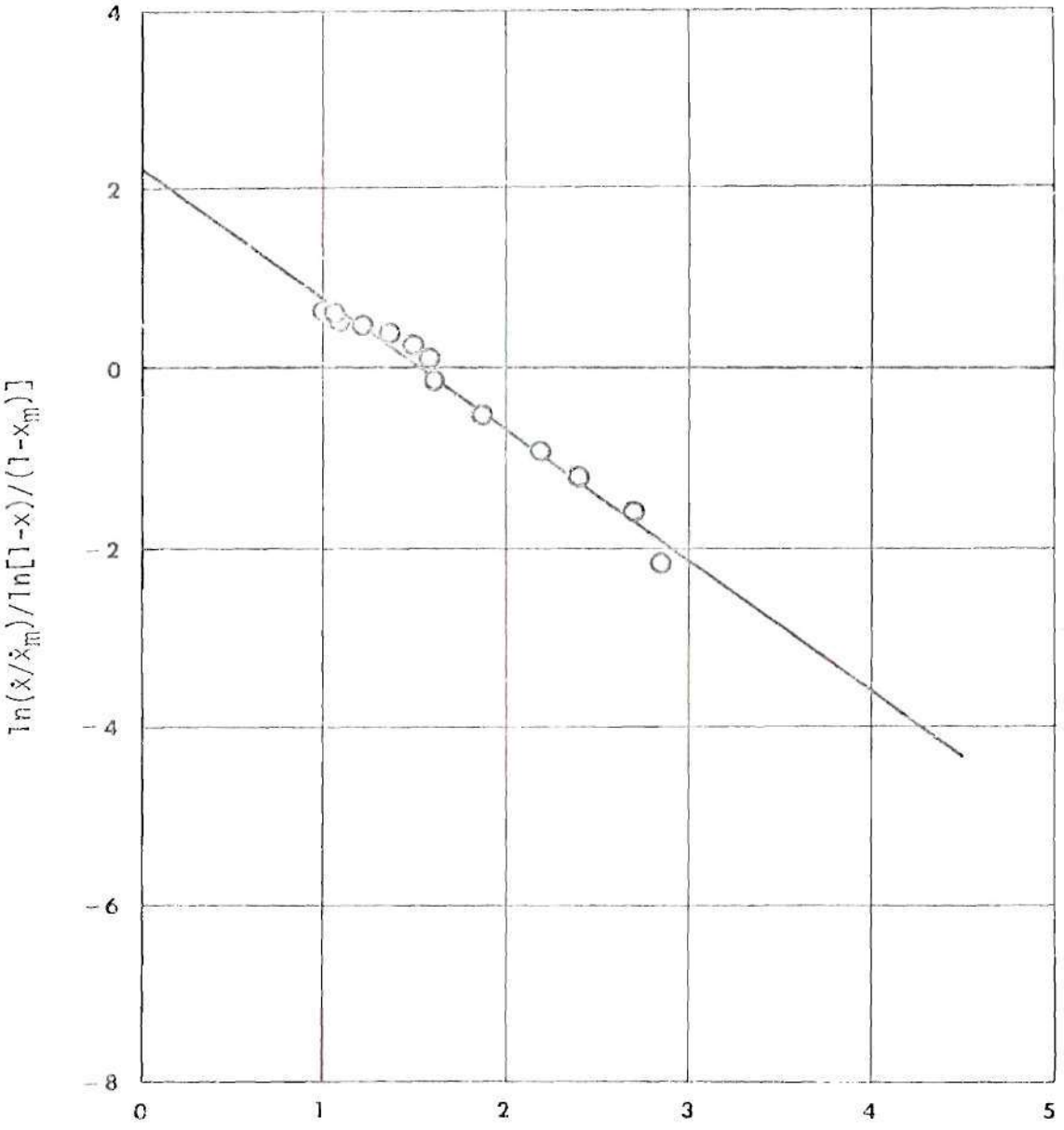


Figure 32. Least - Square Line for GIRCFF Fabric No. 11, Nylon-Acetate Blend, Evaluated by Method I for ϕ = 25°C/min.

(Temp. Range: 28-94°C)

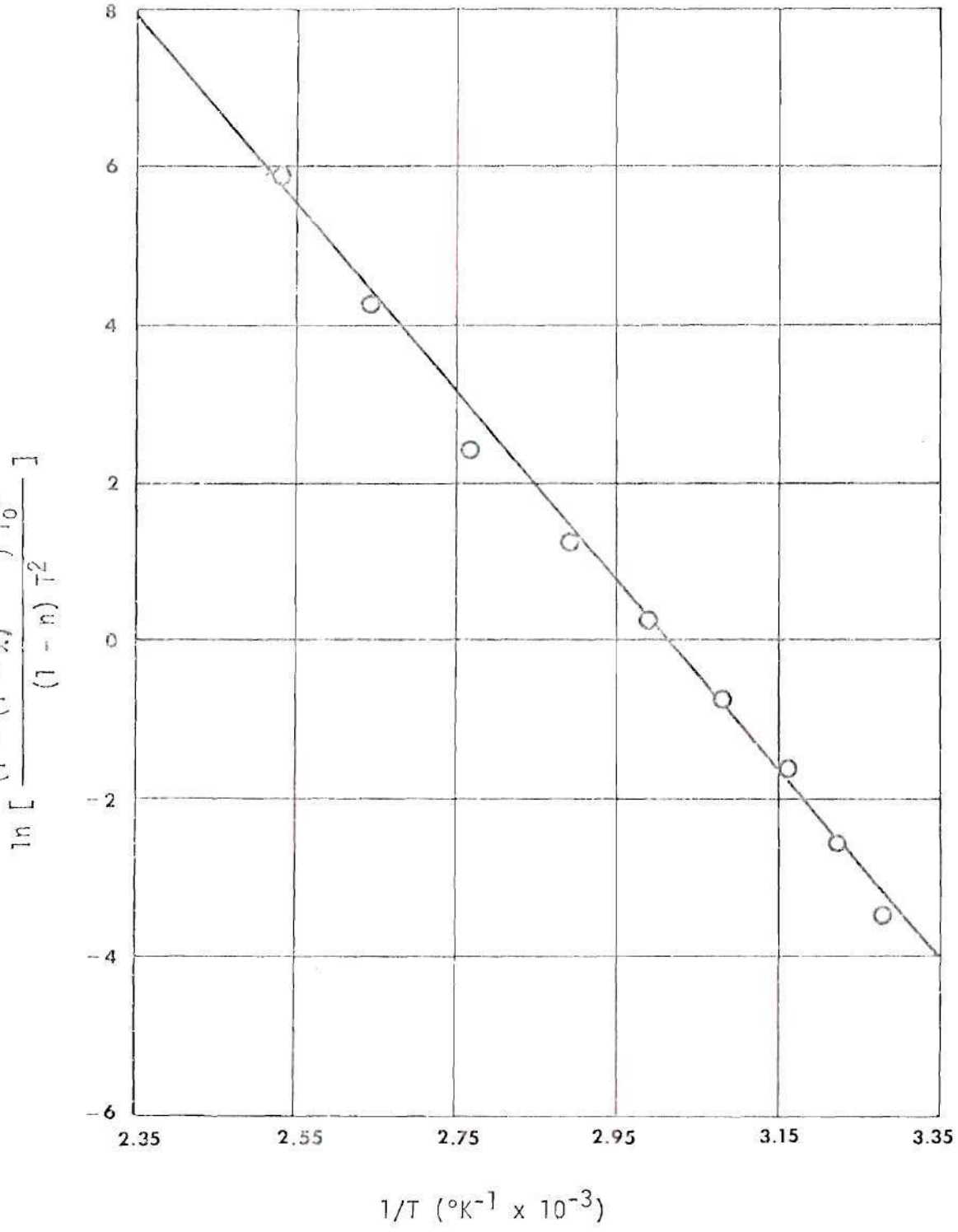


Figure 33. Least - Square Line for GIRCFF Fabric No. 5, Cotton, Evaluated by Method III for ϕ = 25°C/min.

(Temp. Range: 28-149°C)

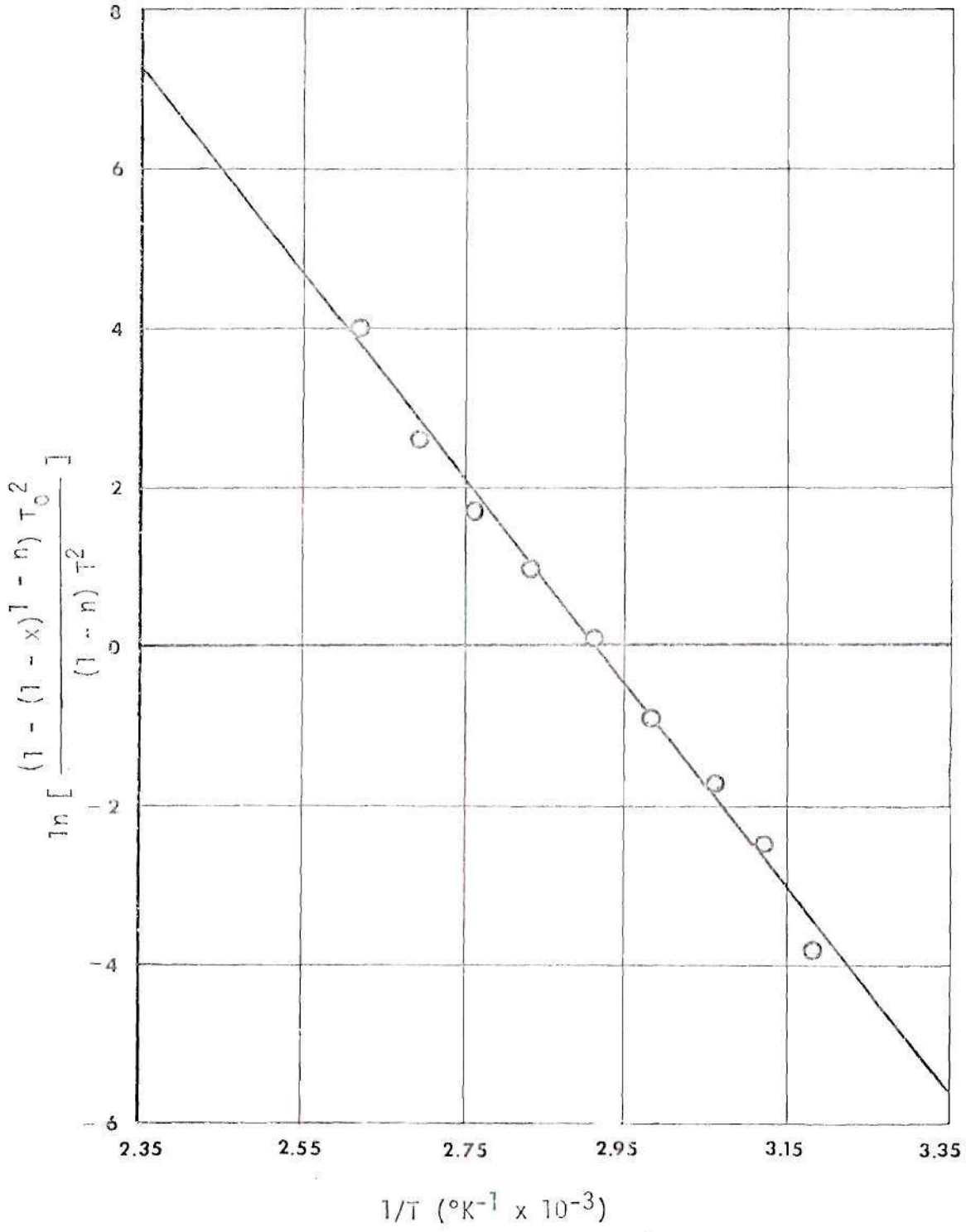


Figure 34. Least - Square Line for GIRCFF Fabric No. 5, Cotton, Evaluated by Method III for ϕ = 10°C/min.

(Temp. Range: 36-120°C)

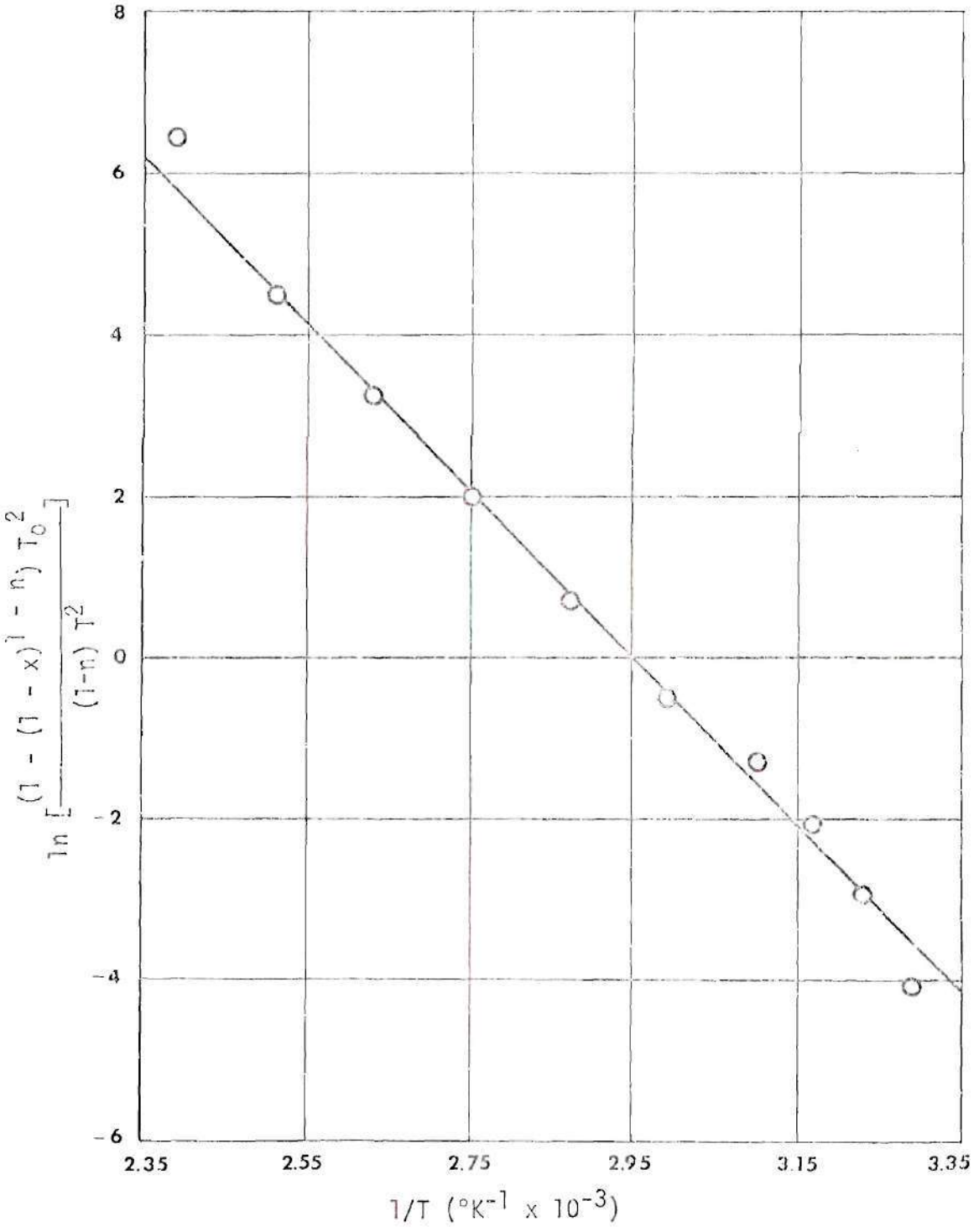


Figure 35. Least - Square Line for GIRCFF Fabric No. 10, Cotton, Evaluated by Method III for ϕ = 25°C/min.

(Temp. Range: 28-169°C)

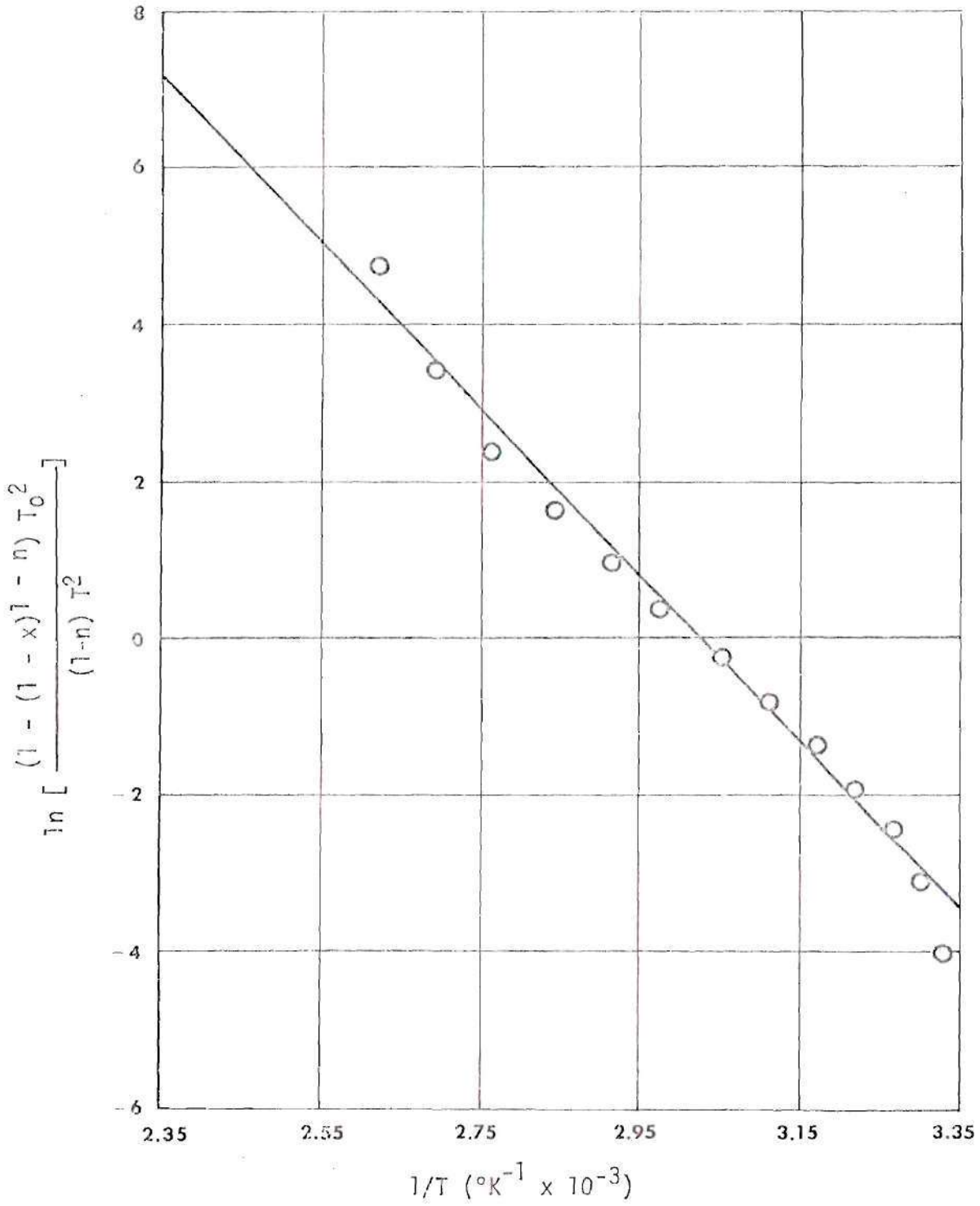


Figure 36. Least - Square Line for GIRCFF Fabric No. 10, Cotton, Evaluated by Method III for ϕ = 10°C/min.

(Temp. Range: 25-120°C)

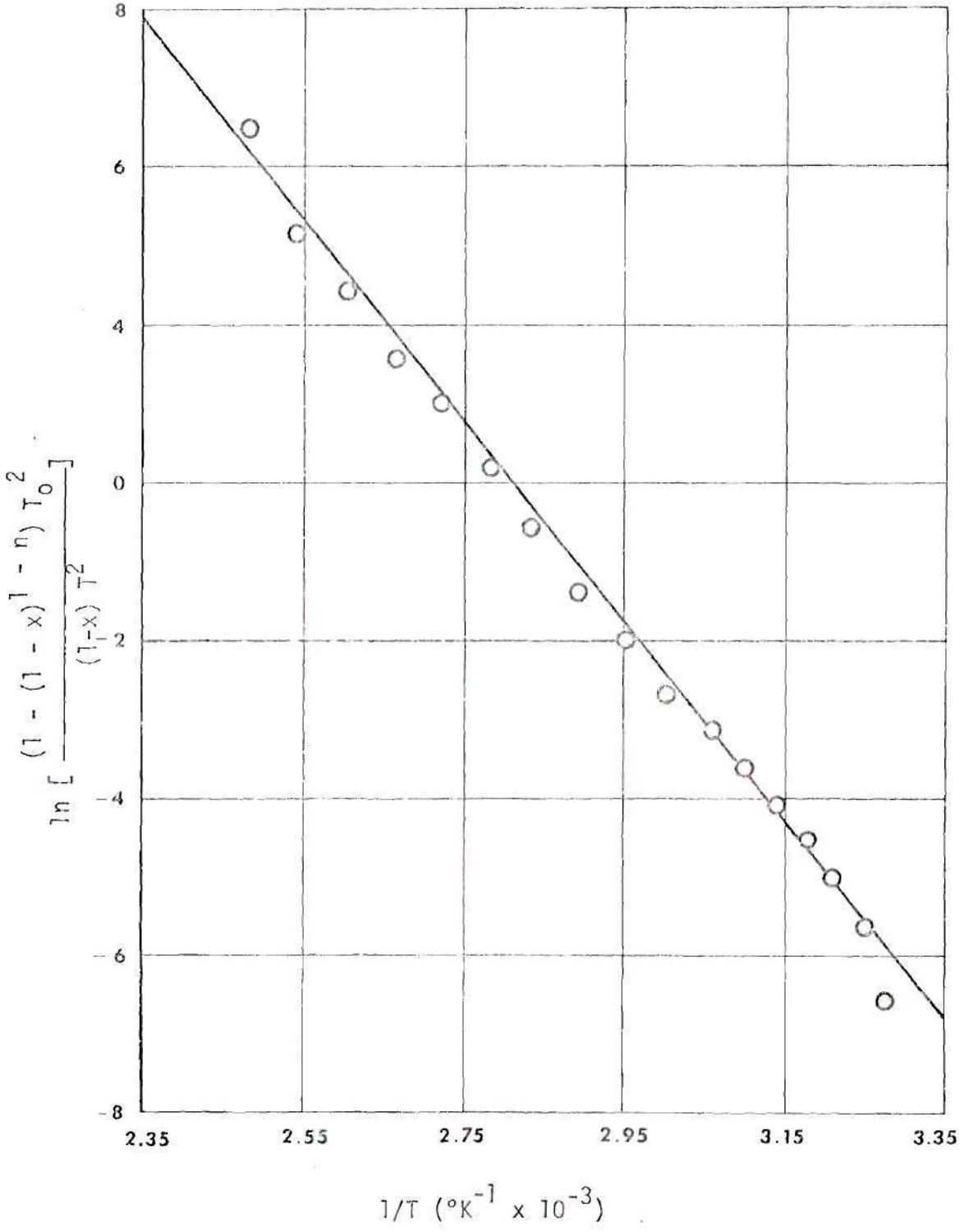


Figure 37. Least - Square Line for GIRCFF Fabric No. 18, Cotton, Evaluated by Method III for ϕ = 25°C/min.

(Temp. Range: 31-140°C)

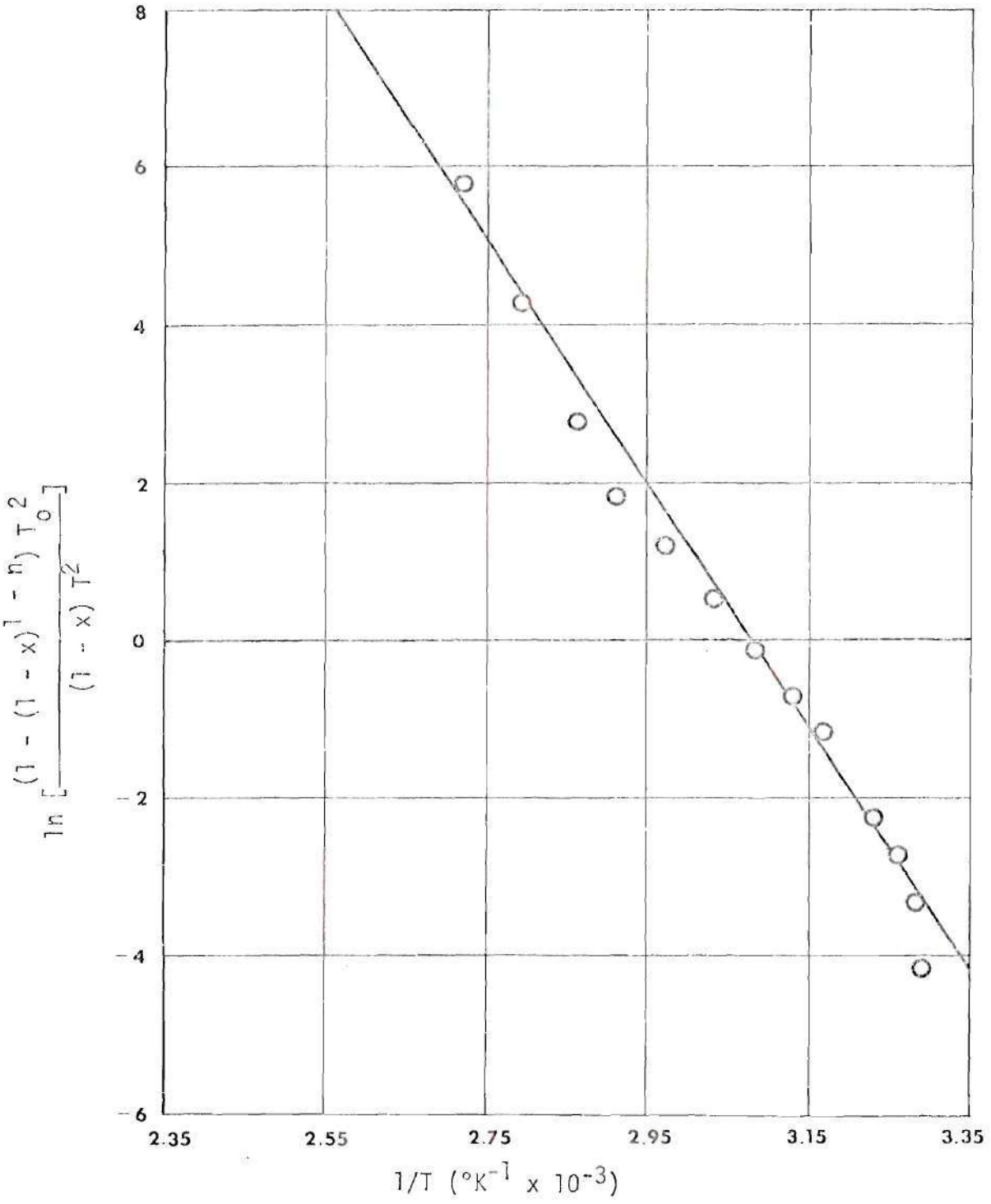


Figure 38. Least - Square Line for GIRCFF Fabric No. 18, Cotton, Evaluated by Method III for ϕ = 10°C/min.

(Temp. Range: 30-103°C)

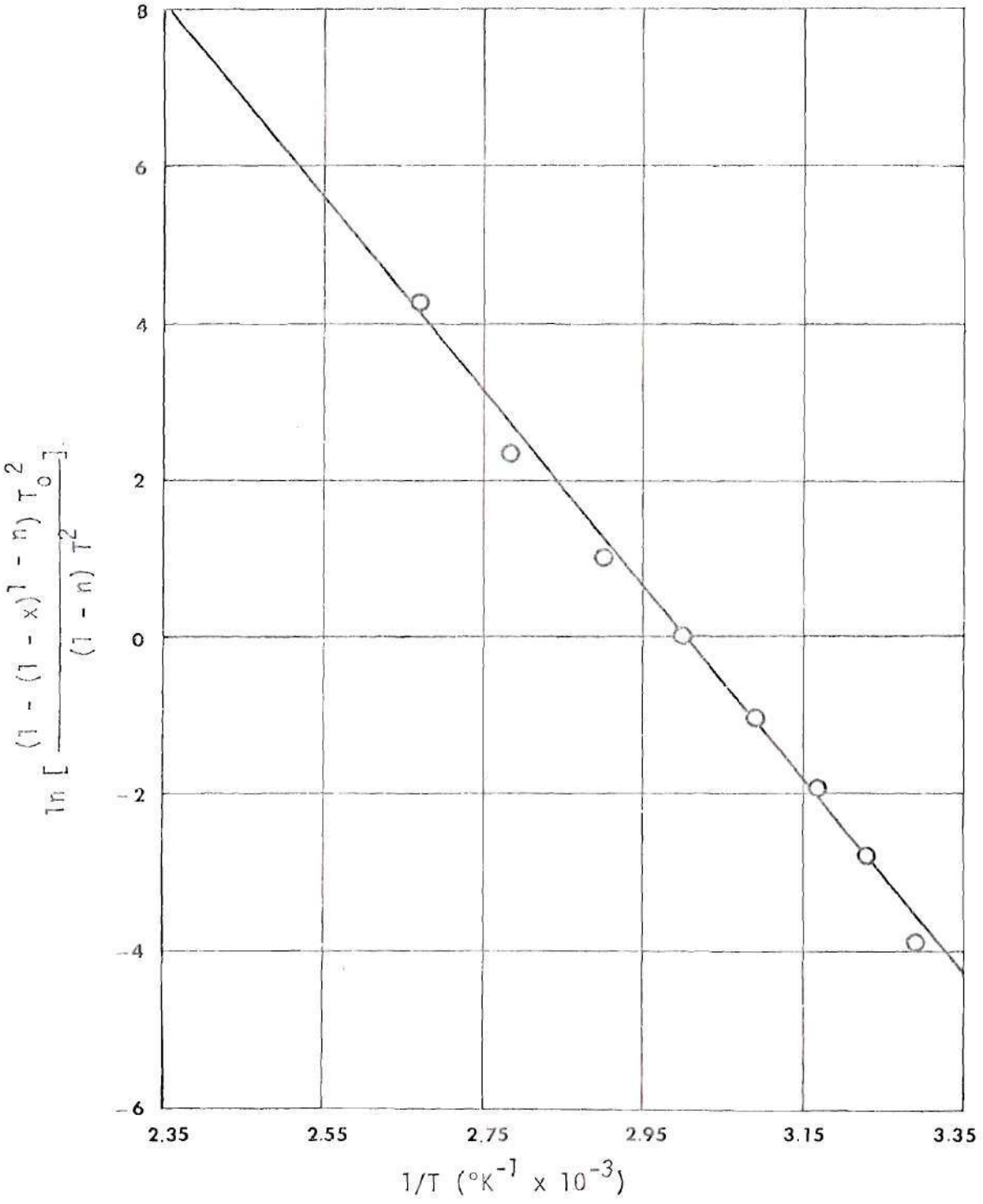


Figure 39. Least - Square Line for GIRCFF Fabric No. 19, Treated Cotton, Evaluated by Method III for ϕ = 25°C/min.

(Temp. Range: 28-120°C)

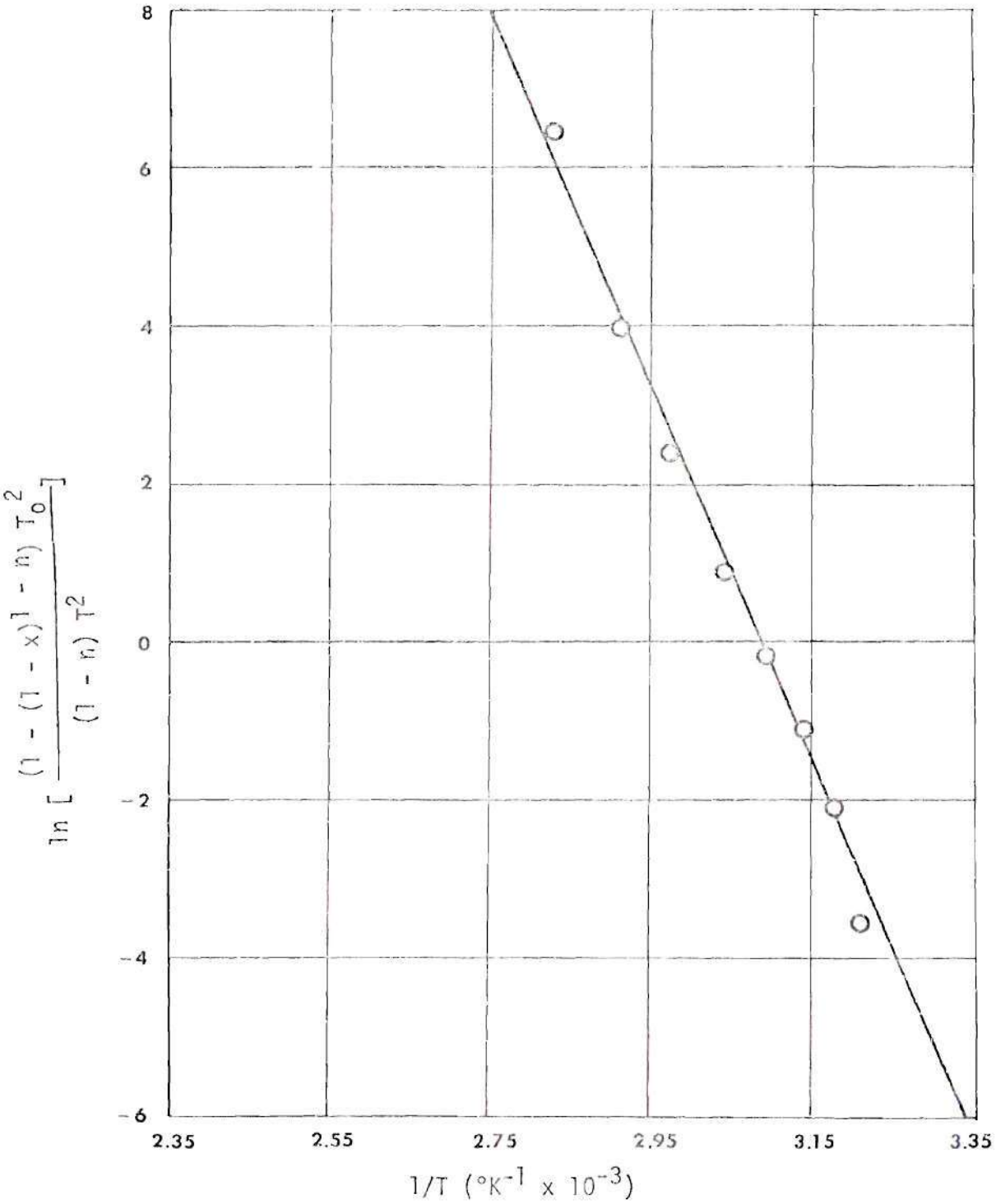
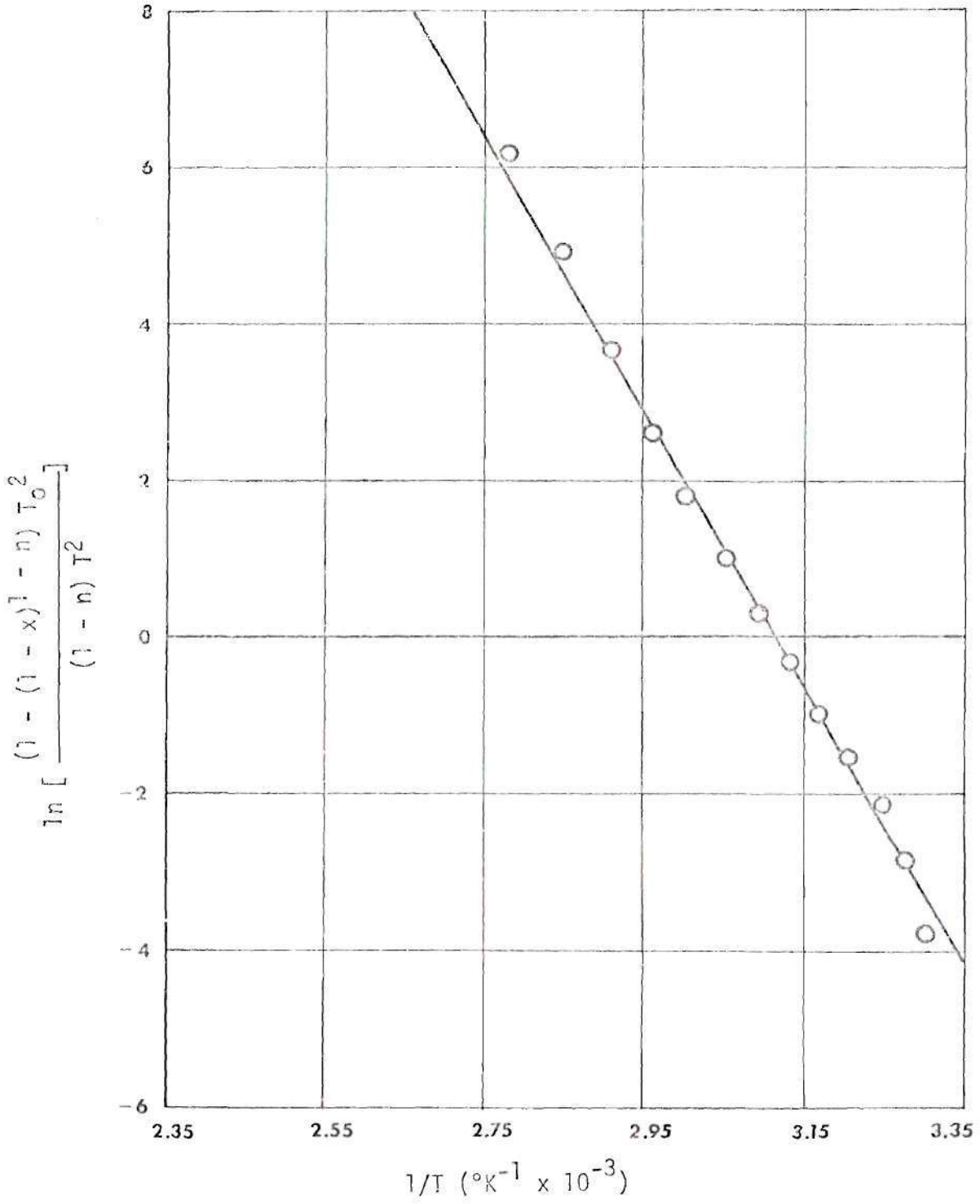


Figure 40. Least-Square Line for GIRCFF Fabric No. 19, Treated Cotton, Evaluated by Method III for ϕ = 10°C/min.

(Temp. Range: 35-90°C)



41. Least - Square Line for GIRCFF Fabric No. 11, Nylon-Acetate Blend, Evaluated by Method III for ϕ = 25°C/min.

(Temp. Range: 28-94°C)

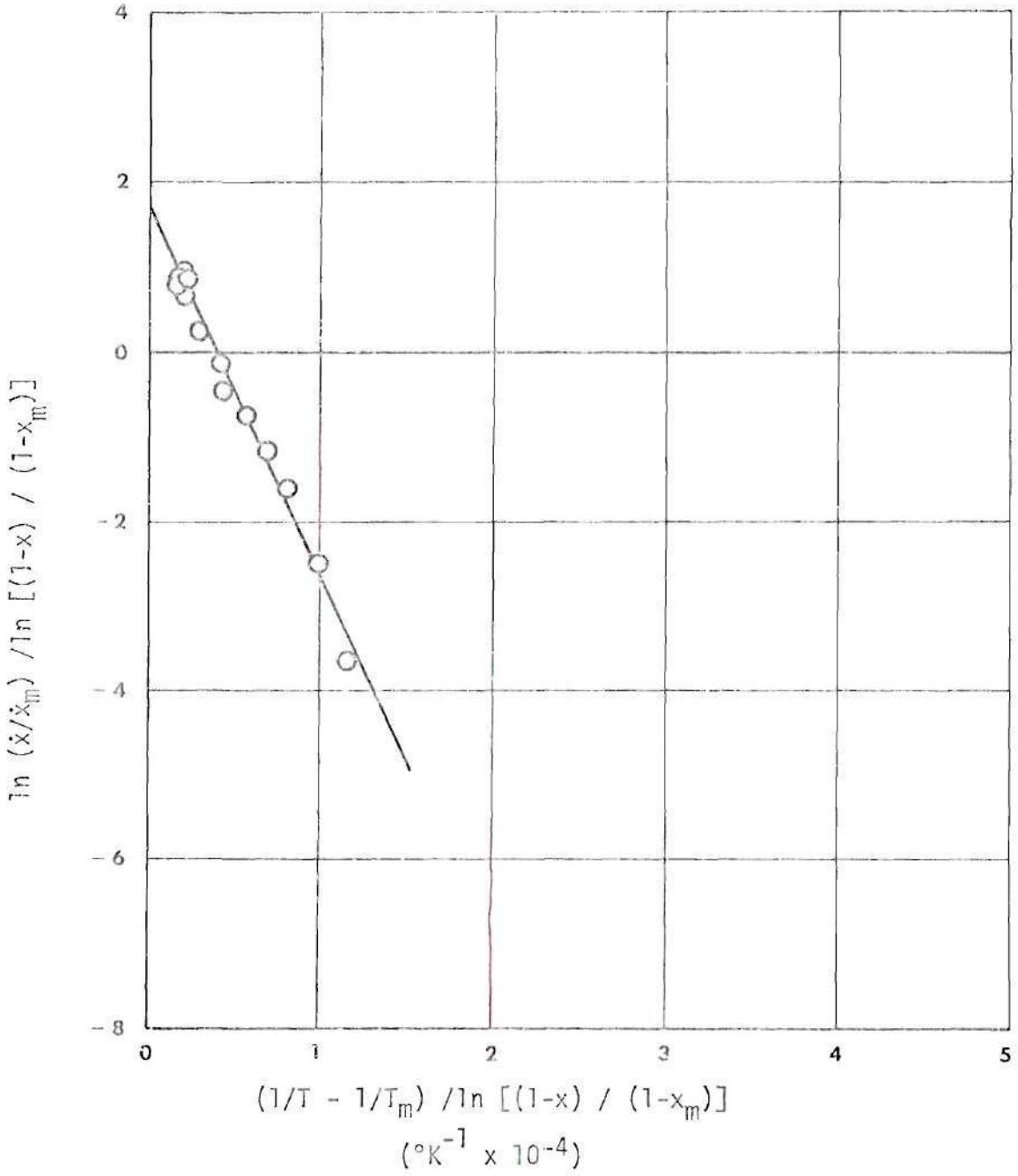


Figure 42. Least - Square Line for GIRCFF Fabric No. 2, Polyester, Evaluated by Method I from McCarter's Data.

(Temp. Range: 414-529°C)

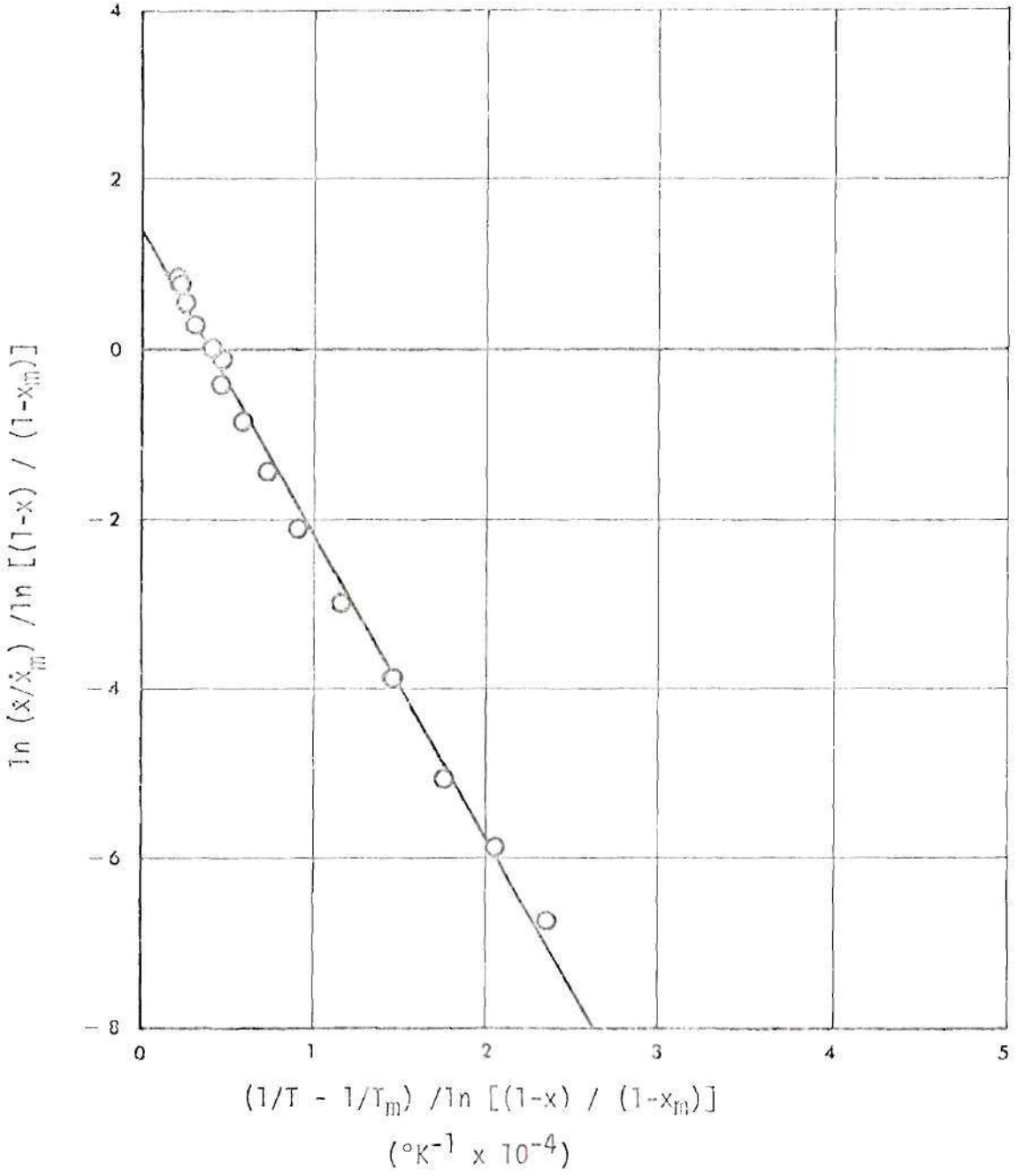


Figure 43. Least - Square line for GIRCFF Fabric No. 5, Cotton, Evaluated by Method I from McCarter's Data.

(Temp. Range: 324-466°C)

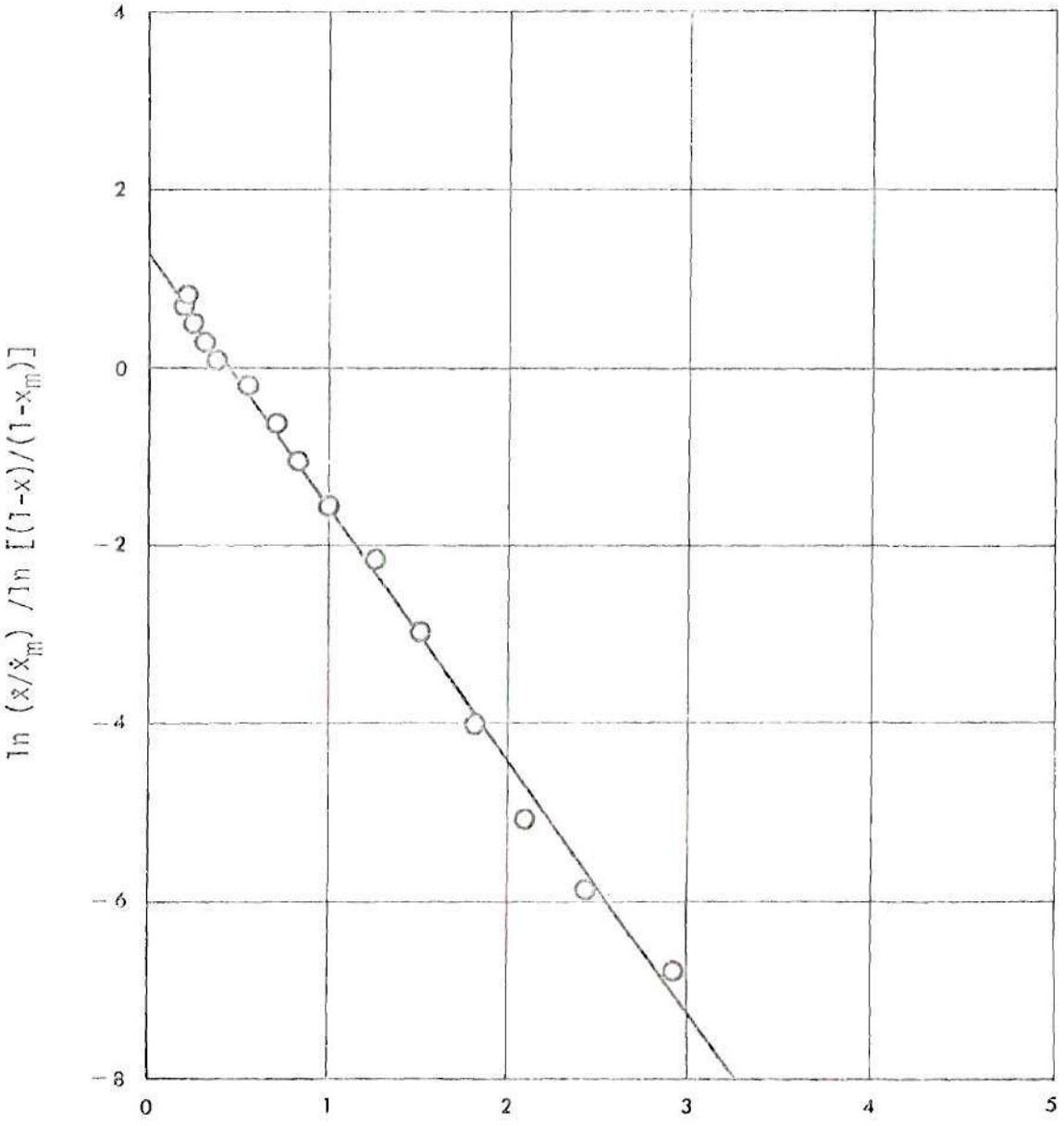


Figure 44. Least - Square Line for GIRCFF Fabric No. 10, Cotton, Evaluated by Method I from McCarter's Data.

(Temp. Range: 319-478°C)

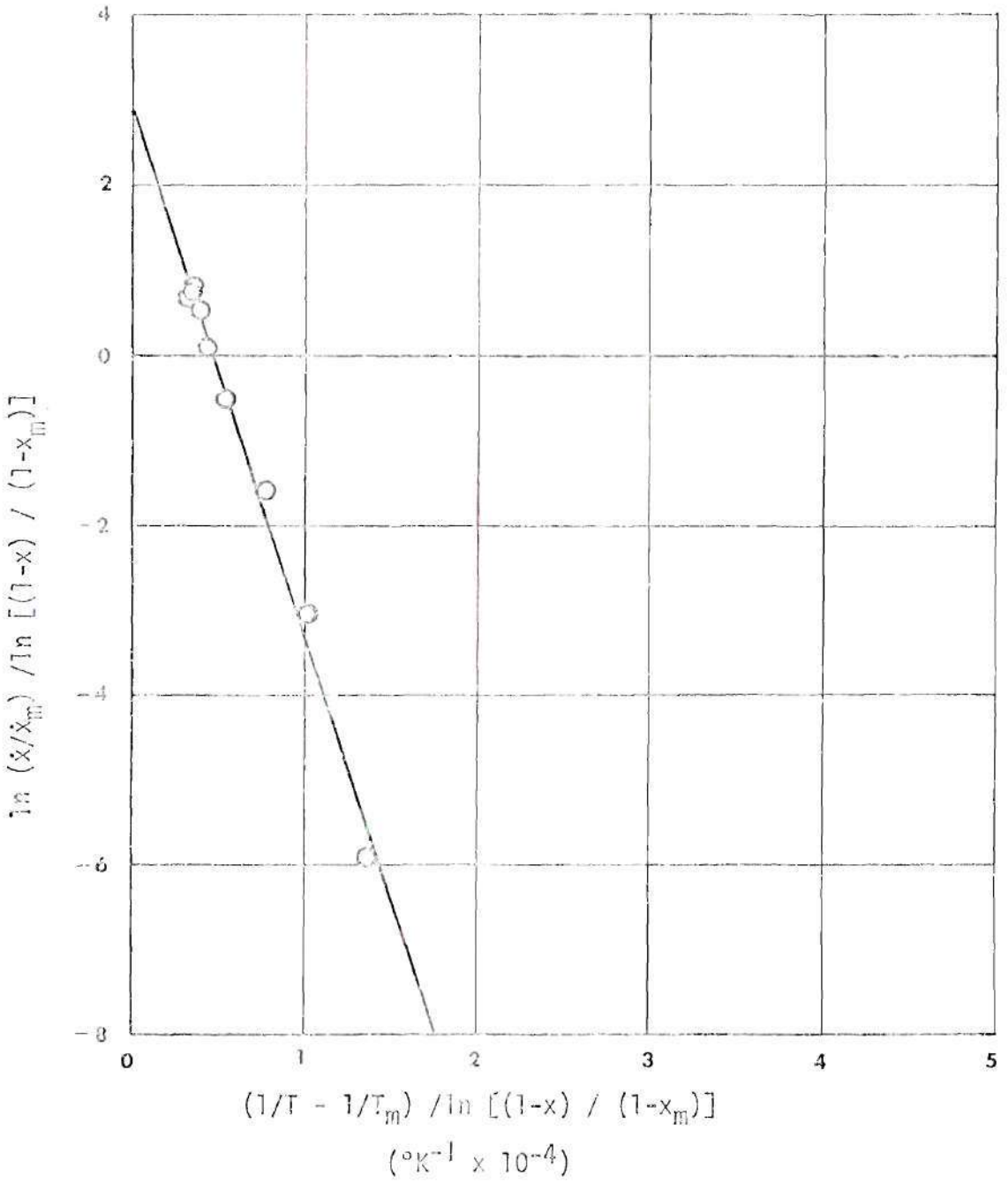


Figure 45. Least - Square Line for GIRCFF Fabric No. 11, Nylon-Acetate Blend, Evaluated by Method I from McCarter's Data.

(Temp. Range: 350-457°C)

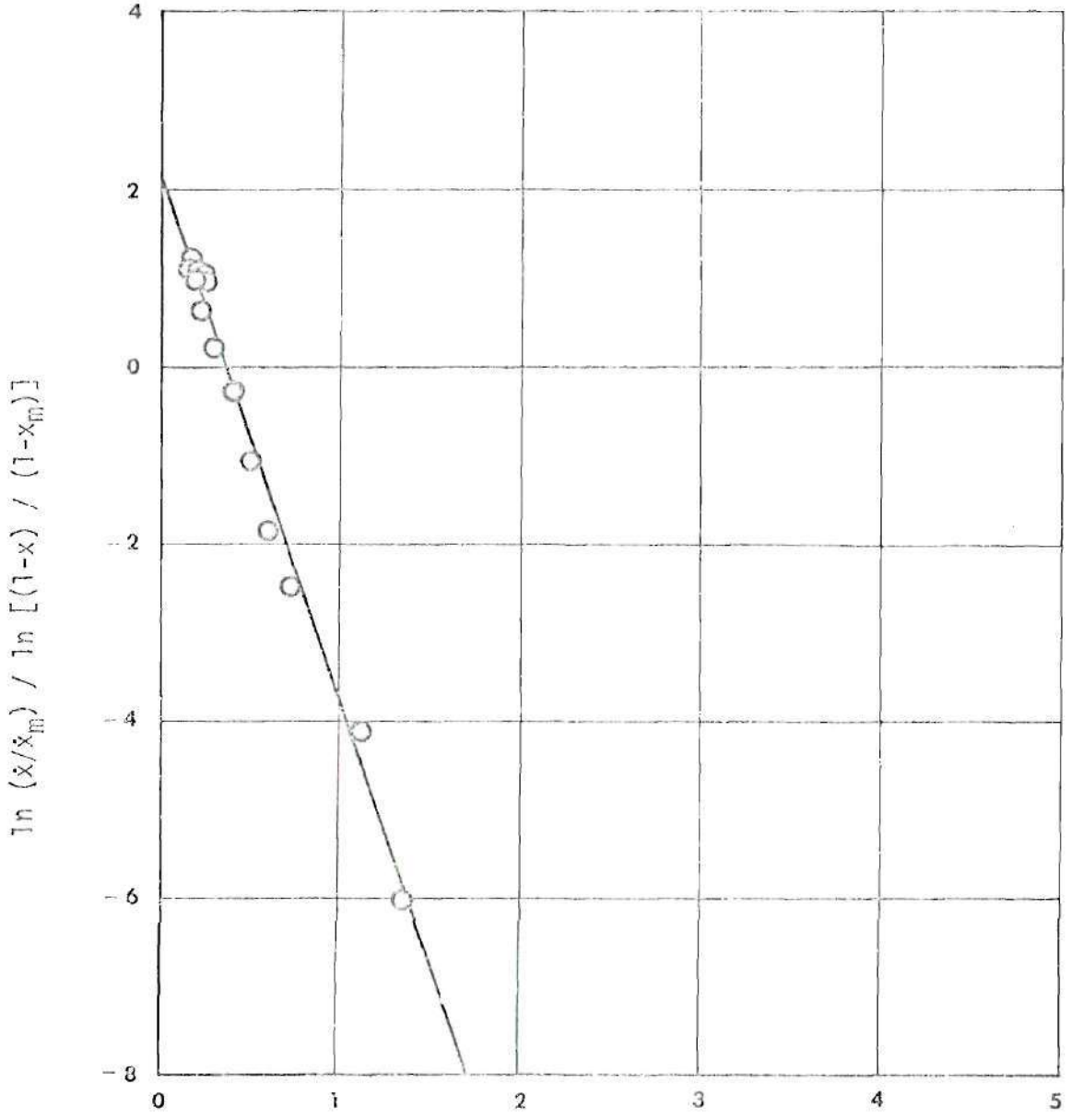


Figure 46. Least - Square Line for GIRCFF Fabric No. 12, Nylon, Evaluated by Method I from McCarter's Data.

(Temp. Range: 404-535°C)

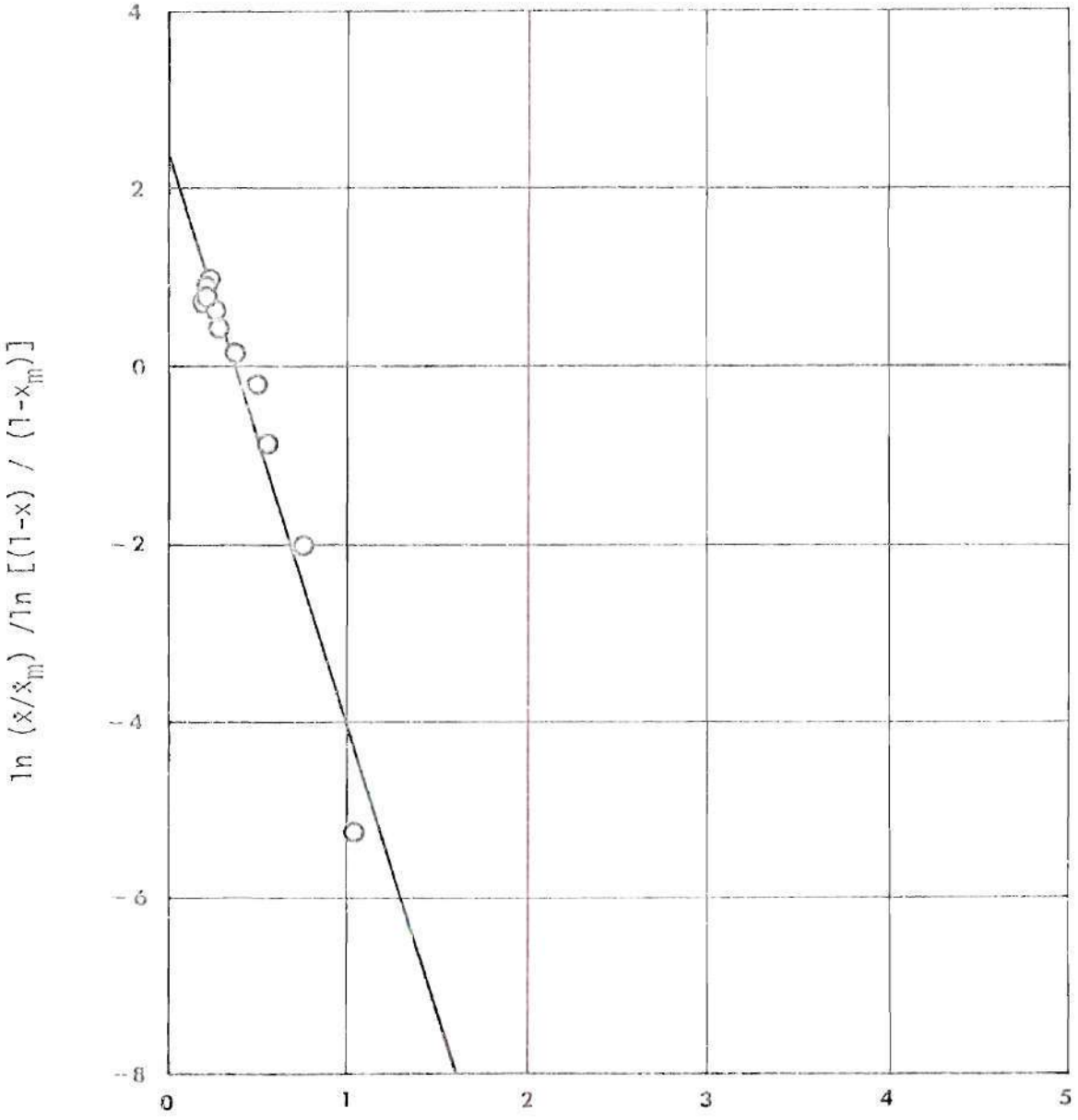


Figure 47. Least - Square Line for GIRCFF Fabric No. 13, Acetate, Evaluated by Method I From McCarter's Data.

(Temp. Range: 360-476°C)

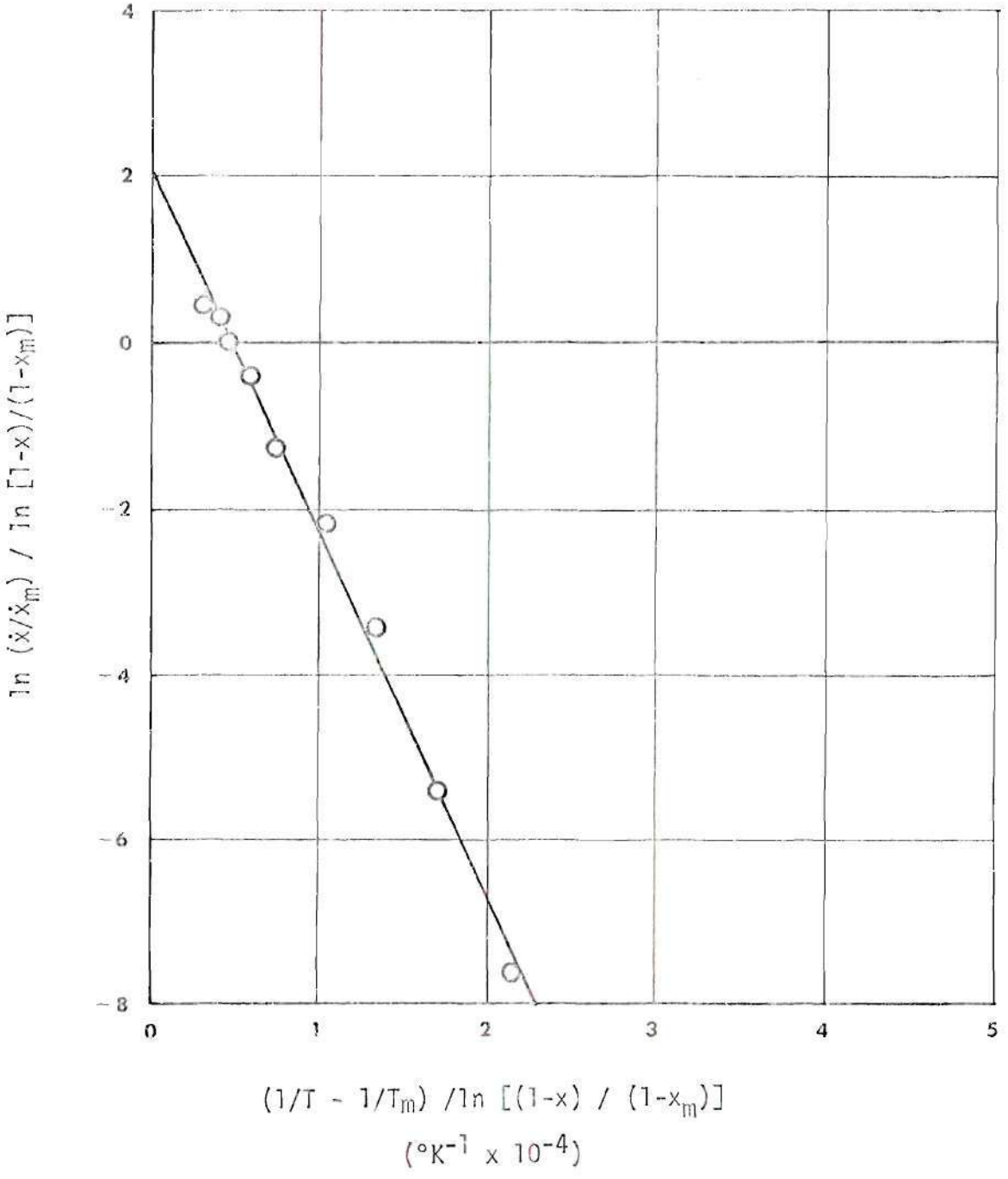


Figure 48. Least - Square Line for GIRCFF Fabric No. 17, Cotton-Polyester Blend, Evaluated by Method I from McCarter's Data.

(Temp. Range: 348-443°C)

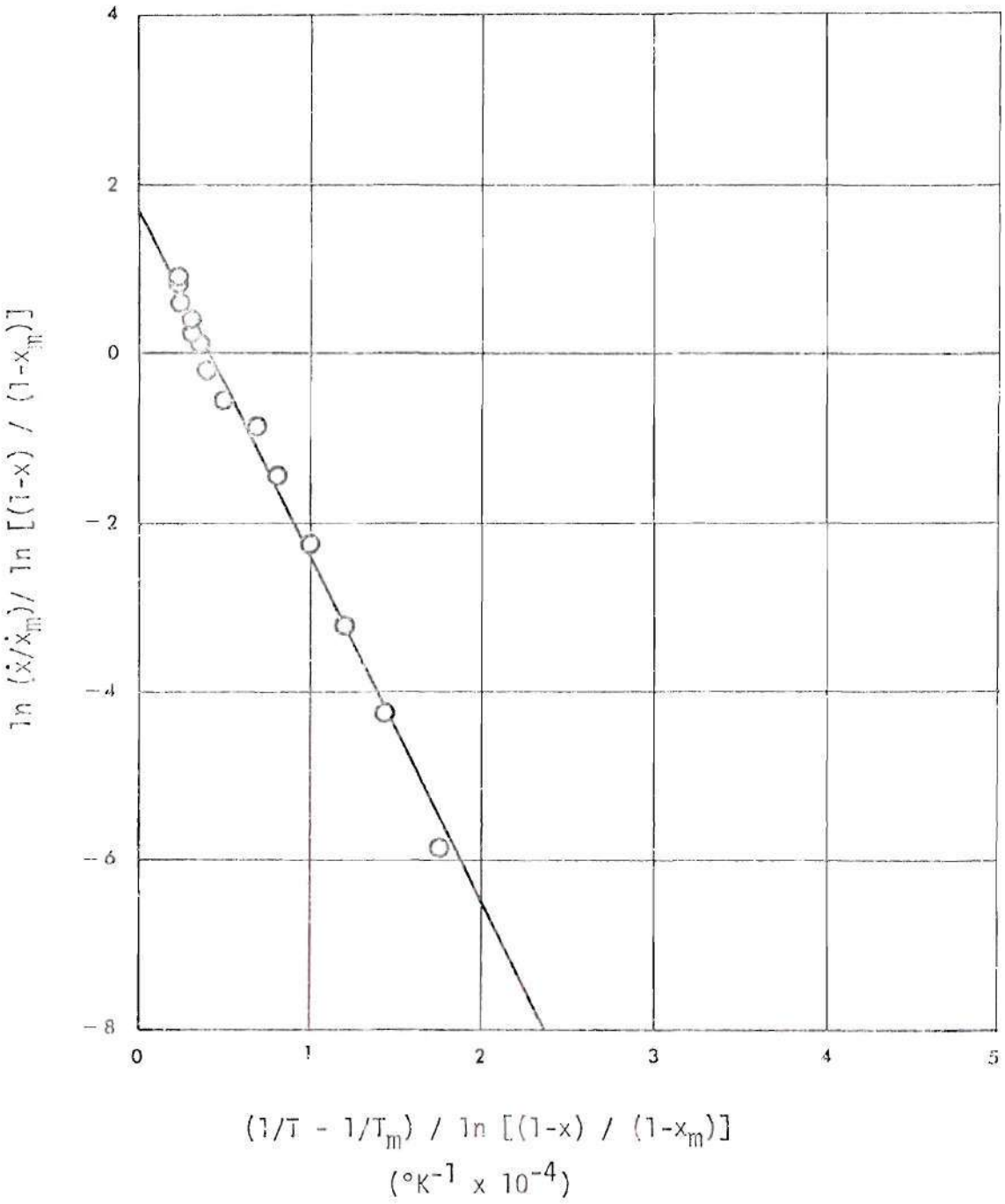


Figure 49. Least - Square Line for GIRCFF Fabric No. 18, Cotton, Evaluated by Method I from McCarter's Data.

(Temp. Range: 333-478°C)

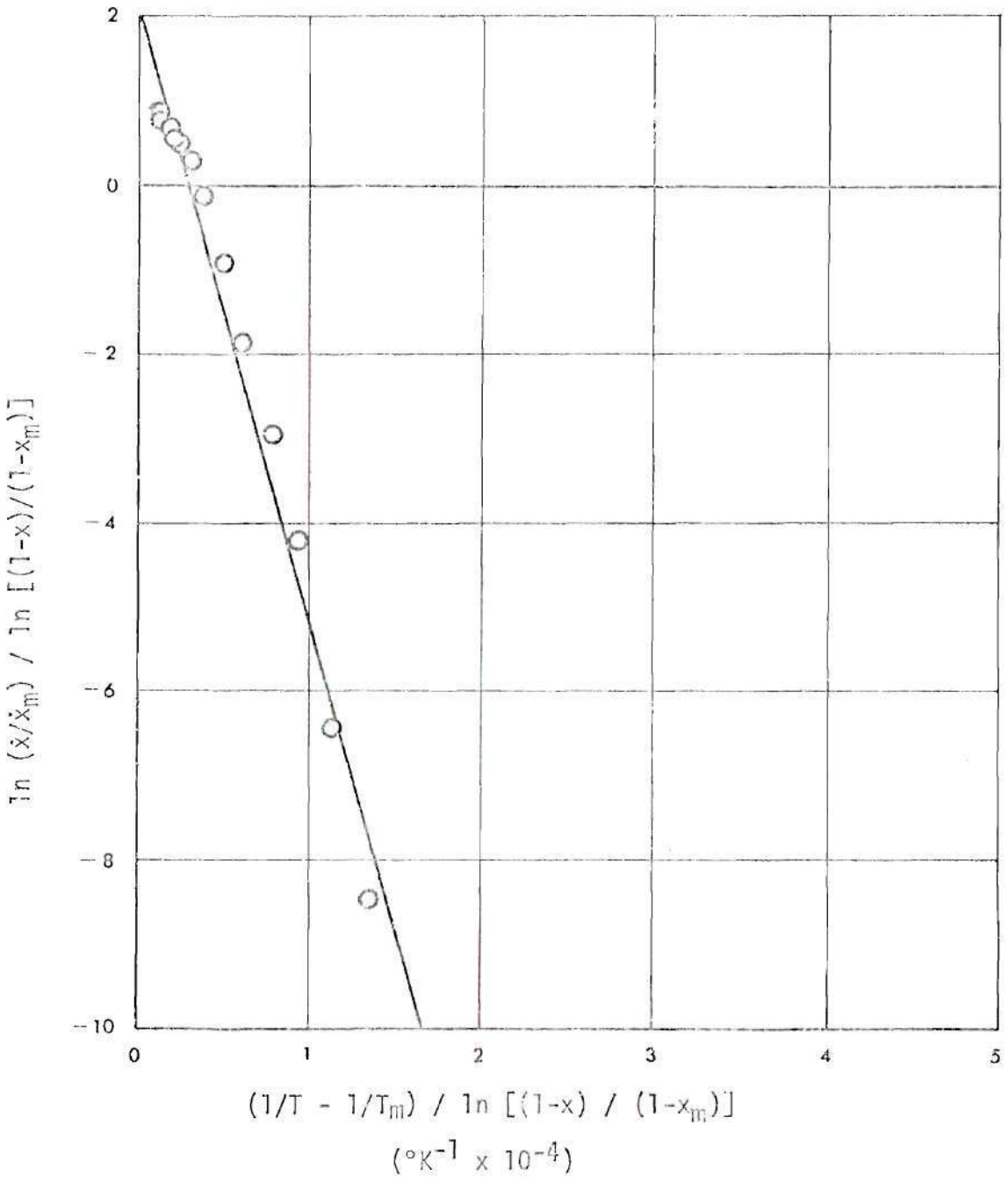


Figure 50. Least - Square Line for GIRCFF Fabric No. 19, Treated Cotton, Evaluated by Method I from McCarter's Data.

(Temp. Range: 319-396°C)

BIBLIOGRAPHY

1. Information Council on Fabric Flammability, Proceedings of Third Annual Meeting, New York City, (1969).

2. Government - Industry Research Committee on Fabric Flammability, "Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods." A work statement prepared by the Research Committee, Dr. E. Passaglia, Chairman, National Bureau of Standards, June 5, 1970.

3. Tribus, M., "Decision Analysis Approach to Satisfying the Requirements of the Flammable Fabrics Act." Paper presented at the Textile and Needle Trades Division, American Society of Quality Control, Greensboro, North Carolina, February 12, 1970.

4. Evans, R. B,, Wulff, W., and Zuber, N., "The Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods," research proposal submitted by the School of Mechanical Engineering, Georgia Insitute of Technology, to the Government Research Committee, July 1970.

5. Wulff, W., Zuber, N., Alkidas, A., and Hess, R. W., "Study of Hazards from Burning Apparel and the Relation of Hazards to Test Methods," Final Report, Georgia Institute of Technology, December 1971.

6. Madorsky, S. L., "Rates of Thermal Degradation of Polystyrene and Polyethylene in a Vacuum," J. Polymer Sci., 9, 133-156 (1952).

7. Mackenzie, R. C., Differential Thermal Analysis Vol. 1, Academic Press, London and New York. (1970).

8. Borchardt, H. J. and Daniels, F., "The Application of Differential Thermal Analysis to the Study of Reaction Kinetics," J. Am. Chem. Soc., 79, 41-46 (1957).

9. Schwenker, R. F., Beck, L. R. and Zuccarello, R. K., "Applications of Differential Thermal Analysis and Dynamic Thermogravimetric Analysis in Textile Research," Am. Dyestuff Rept., 53, 817-827 (1964).

10. Akita, K. and Kase, M., "Determination of Kinetic Parameters for Pyrolysis of Cellulose and Cellulose Treated with Amononium Phosphate by Differential Thermal Analysis and Thermogravimetric Analysis," J. Polymer Sci.: Part A-1, 5, 833-848 (1967).

11. Freeman, E. S. and Carroll, B., "The Application of Thermoanalytical Techniques to Reaction Kinetics. The Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate," J. Phy. Chem., 62, 394-397 (1958).

12. Coats, A. W. and Redfern, J. P., "Kinetic Parameters from Thermogravimetric Data," Nature, 201, 68-69. (1964).

13. LeChatelier, H., "The Action of Heat on Clay," Bull. Soc. Franc. Minera'l, 10, 204-11 (1887).

14. Roberts - Austen, S. C., "Fifth Report tbethe Alloys Research Committee," Proc. Inst. Mech. Engrs. (London), 1, 35-102 (1899).

15. Carpenter, H. C. H. and Keeling, B. F. E., "The Range of Solidification and Critical Ranges of Iron-Carbon Alloys," J. Iron Steel Inst. (London), 65(1), 224-42 (1904).

16. Carpenter, H. C. H., "The Types of Structure and the Critical Ranges of High-Speed Tool Steels Under Varying Thermal Treatment," Collected Researchers, Nat'l. Phys. Lab. (London), 2, 52-89 (1907).

17. Burgess, G. K., "On Methods of Obtaining Cooling Curves," Electrochem. Metal. Ind., 6, 366-71 (1908).

18. Burgess, G. K. and LeChatelier, H., The Measurement of High Temperatures, John Wiley & Sons, New York (1912).

19. Smothers, W. J. and Chiang, Y., Handbook of Differential Thermal Analysis, Chemical Publishing Co., Inc. New York (1966).

20. Grimshaw, R. W., Heaton, E., and Roberts, A. L., "The Constitution of Refractory Clays. Part II," Trans. Brit. Ceram. Soc., 44, 76-92 (1945).

21. Godfrey, L. E. A., "Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) Studies of Flame Retardant Rayon Fibers," Text. Res. J., Feb. 1970, 116-126.

22. Loughlin, J. et al., "Differential Thermal Analysis in Predicting Fiber Blend and Probing Fiber Properties," Am. Dyestuff Rept., Feb. 1956, 25-38.

23. Ramiah, M. V., "Thermogravimetric and Differential Thermal Analysis of Cellulose, Hemicellulose, and Lignin," J. Appl. Polymer Sci., 14, 1323-1337 (1970).

24. Schwenker, R. F. and Zuccarello, R. K., "Differential Thermal Analysis of Synthetic Fibers," J. Polymer Sci.: Part C, 6, 1-16 (1964).

25. Hendrix, J. E. et al., "Pyrolysis and Combustion of Cellulose. I. Effects of Triphenyl Phosphate in the Presence of Nitrogenous Bases," J. Appl. Polymer Sci., 14, 1701-1723 (1970).

26. Perkins, R. M., Drake, G. L. and Reeves, W. A., "DTA and TGA Studies of Flame-Retardant Fabrics," J. Appl. Polymer Sci., 10, 1041- 1066 (1966).

27. Tang, W. K. and Neill, W. K., "Effect of Flame Retardants on Pyrolysis and Combustion of α - Cellulose," J. Polymer Sci.: Part C, 6, 65-61 (1964).

28. Arens, P. L., A Study of the Differential Thermal Analysis of Clays and Clay Minerals, Gravenhage, Wagemingen, Netherlands (1951).

29. Grimshaw, R. W. and Roberts, A. L., "Quantitative Determination of Some Minerals in Ceramic Materials by Thermal Means." Trans. Brit. Ceram. Soc., 52, 50-67 (1953).

30. Sabatier, I. G., "Measure of the Heats of Transformation by Differential Thermal Analysis," Bull. Soc. Frame. Minera'l, 77, 953-68 (1954).

31. Speil, S. et al., "Differential Thermal Analysis. Its Application to Clays and Other Aluminous Minerals," Tech. Pap. Bur. Mines, Wash., No. 664, 1-37 (1945).

32. Nagasawa, K., "Differential Thermal Analysis Studies on the High-Low Inversion of Vein Quartz in Japan," J. Earth Sci., Nagoya Univ., 1, 156-76 (1953).

33. Berg. L. G., "Introduction to Thermal Analysis," Izd. Akad. Nauk USSR, Moscow (1961).

34. Bollin, E. M. and Kerr, P. F., "Differential Thermal Pyrosynthesis," Am. Mineralogist, 46, 823-58 (1961).

35. American Association of Textile Chemists and Colorists Monograph Number 3, Analytical Methods for a Textile Laboratory, AATCC, Research Triangle Park, North Carolina (1968).

36. Vold, M. J., "Differential Thermal Analysis," Anal. Chem., 21, 683-8 (1949).

37. Soule', J. L., "Quantitative Interpretation of Differential Thermal Analysis," J. Phys. Radium, 13, 516-20 (1952).

38. Kissinger, H. E., "Reaction Kinetics in Differential Thermal Analysis," Anal. Chem., 29, 1702-6 (1957).

39. Turner, W. N. and Johnson, F. C., "The Pryolysis of Acrylic Fiber in Inert Atmosphere," J. Appl. Polymer Sci., 13, 2073-84 (1969).

40. Gilliland, B. F. and Smith, B. F., "Flame-Retardant Properties and Thermal Behavior of Selected Flame-Retardant Cotton Fabrics," J. Appl. Polymer Sci., 16, 1801-16 (1972).

41. Honda, K., "A Thermobalance," Sci. Rept. Tohoka Imp. Univ., 4, 97-103 (1915).

42. Guichard, M., "The Rate of Dehydration at Increasing Temperature," Bull. Soc. Chim. France, 37, 62-7 (1925).

43. Duval, C., "Sur la Thermogravime'tric des Pre'cipite's Analytiques," Anal. Chim. Acta., 1, 341-4 (1947).

44. Anderson, D. A. and Freeman, E. S., "The Kinetics of the Thermal Degradation of the Synthetic Styrenated Polyester, Laminac 4116," J. Appl. Polymer Sci., 1, 192-199 (1959).

45. Slade, P. E. and Jenkins, L. T., Techniques and Methods of Polymer Evaluation, Vol. I, Marcel Dekker, Inc. New York (1966).

46. Newkirk, A. E., "Thermal Methods of Analysis," Anal. Chem., 32, 1558-63 (1960).

47. McCarter, R. J., "Apparatus for Rate Studies of Vapor Producing Reactions," NBS Special Publication 338, 137-149 (1971).

48. McCarter, R. J., "Report on the Thermal Analysis of GIRCFF Fabrics," NBS Report 10 846, May 11, 1972.

49. Chatterjee, P. K., "Application of Thermogravimetric Techniques to Reaction Kinetics," J. Polymer Sci.: Part A-1, 6, 3217-33 (1968).

50. Doyle, C. D., "Kinetic Analysis of Thermogravimetric Data," J. Appl. Polymer Sci., 5, 285-292 (1961).

51. Farmer, R. W., "Thermogravimetry of Plastics; Part 1: Empirical Homogeneous Kinetics," ASD-TDR-62-1043, Part 1 (1963).

52. Reich, L., "Estimation of Kinetic Parameters from Thermogravimetric Traces," J. Appl. Polymer Sci., 9, 3033-39 (1965).

53. Sharp, J. H. and Wentworth, S. A., "Kinetic Analysis of Thermogravimetric Data," Anal. Chem., 41, 2060-2 (1969).

54. Chatterjee, P. K., "Thermogravimetric Analysis of Cellulose," J. Polymer Sci.: Part A-1, 6, 3217-33 (1968).

55. Madorsky, S. L., Hart, V. E., and Strauss, S., "Thermal Degradation of Cellulose Materials," J. Res. NBS, 60, 343-9 (1958).

56. Bolz, R. E. and Tuve, G. L., editors, Handbook of Tables for Applied Engineering Science, Chemical Rubber Co., Cleveland (1970).

57. Hamby, D. S., ed., American Cotton Handbook, Vol. 1, Interscience Pub., New York (1965).

58. Cook, J. G., ed., Handbook of Textile Fibers, Merrow Pub. Co., Herts, England (1968).

59. Ke, B. and Sisko, A. W., "Differential Thermal Analysis of High Polymers. III. Polyamides," J. Polymer Sci., 50, 87-98 (1961).

60. Rossini, F. D., NBS Circular 500, National Bureau of Standards, Washington, D.C. (1952).